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THE ACADÉMIE DES SCIENCES IN THE ROYAL LIBRARY AT VERSAILLES IN 1671

EDITOR'S OUTLOOK

THE frontispiece of this issue of the JOURNAL OF CHEMICAL EDUCATION presents, in a reproduction of a copper-plate engraving by Sebastien Le Clerc, the earliest representation of an actual meeting of a learned society. It has for its center the figures of Louis XIV and Colbert, for it was under the patronage of the Grand Monarch and at the instance of his minister that l'Académie des Sciences received official status as an organization, although for many years, certainly as early as 1640, it had existed informally in an association of men of similar or allied scientific interests, among whom the names of Descartes, and Blaise and Étienne Pascal are prominent. Its membership was at no time nationally confined, Sir Isaac Newton having been one of its early foreign associates. Royal grants were made to support the work of the academicians and the royal library at Versailles was opened to their sessions, the first of which was held there on December 22, 1666.

L'Académie des Sciences

After the death of Colbert the work of the academy was diverted from pure science to the practical details of constructing the new paradise at Versailles. The suggestion of this task is artfully introduced into the background of Le Clerc's picture, while its foreground is alive with symbols of the occupations and interests of the academy, the materials or instruments of mathematics, engineering, geography, zoölogy, botany, astronomy, and anatomy. Of particular moment among these is the air-pump invented by Robert Boyle in 1660, which appears on the table at the left of the picture.

In 1699 the academy was reconstructed and reverted to its primary devotion to pure research. Its membership was limited to twenty-five, ten honorary and fifteen working members, three places among the latter being assigned permanently to chemists. In 1793, in the political and social chaos of the time, the organization was suppressed, but it was revived in 1816 as a branch of the Institut National. Lavoisier in the eighteenth century kept chemistry in the forefront of the academy's titles to eminence, and in a less remote generation its roster included the physicists Ampère, Arago, Fresnel, and Biot, and the chemists Gay-Lussac and Thénard, as makers of scientific history.

Le Clerc's engraving perpetuating an early meeting of the academy appears opposite the title page of a sumptuously produced work of science, *Mémoires pour servir à l'histoire des animaux* (*Paris à l'imprimerie royale*), most of the copies of which were distributed as personal gifts by Louis XIV.

The JOURNAL OF CHEMICAL EDUCATION *gratefully acknowledges the courtesy of* DR. CHARLES SINGER, *of London, England, president of the Second International Congress of the History of the Science and Technology, for the foregoing picture and for much of the information regarding it upon which the above sketch is based.*

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Professional Altruism

A DECADE AGO the cry for popularizers of chemistry was ringing throughout the United States. That cry has been nobly answered. Newspaper items, magazine articles, and volumes of various degrees of weight and importance have flowed from the presses. The radio and the moving picture have played their parts. Today, while the hypothetical average American still knows practically no chemistry, he is perceptibly "chemistry-conscious" and he knows at least something *about* chemistry. We have at other times echoed in these columns the hope and belief that the time is now ripe when we can begin to experiment with means of teaching him a little chemistry as well as a lot about chemistry.

But there is also reason to feel that the need for some missionary work of a similar kind within our own ranks exists. The field of chemistry expands at an appalling rate. A knowledge of physics and of mathematics becomes more and more essential to productive work of significant caliber or indeed to mere scholarship. Specialties multiply. The average chemist or teacher of chemistry knows less and less of what is going on outside the narrow confines of his own special interests.

There are those who hold that this state of affairs is inevitable and will inevitably grow worse and that nothing can be done about it. We are not altogether of that mind. We believe that a great service to chemistry can be performed by men of special interests and special learning who have the ability and can find the will to construct elementary reviews of the theories and accomplishments within their own fields. Men who are not afraid to go into elementary details for fear of saying something obvious—who are willing to write down to the educational level of the college senior, which is just about where most chemists remain concerning all of chemistry except their own specialties.

Fortunately there are already a few who see the need and who have the altruism to undertake the labor and to expend the time necessary. May their tribe increase, and that right rapidly.

As this number goes to press the judges of the 1930-31 American Chemical Society Prize Essay Contests announce that the winners in the College Freshman and in the Normal School and Teachers' College classes have been selected. The announcement of the names of the winners has been inserted at the end of the Contemporary News section (page 1235).

MAN-MADE GEMS

FRANK B. WADE, SHORTRIDGE HIGH SCHOOL, INDIANAPOLIS, INDIANA*

Early attempts to make artificial precious stones resulted in minute rubies and sapphires. Solvents, such as fused borax, were used and either the temperature-gradient method or the method of evaporation of the solvent was followed. Subsequently double decompositions were employed and Fremy, about 1890, succeeded in getting rubies of about one-third of a carat. About this time numerous "reconstructed" rubies were made and marketed, the method consisting in fusing together small fragments of natural ruby crystals. The product was a single crystal and had the properties of the natural stone. The modern synthetic stones were first produced by Verneuil. His method forces the proper material through an inverted oxy-hydrogen gas flame as a fine dust, which fuses and crystallizes as a single crystal above the first "seed" crystal to form on a refractory support below.

. . . . . .

John Ruskin, in his "Ethics of the Dust," advises us, "Absolutely search out and cast aside all manner of false, or dyed or altered gems." Consequently, this article will not consider the many successful imitations which men have made since very early times, but, instead, will attempt to give a brief and elementary account of the story of man's achievements in the actual production of genuine (but not natural) gem stones.

As most high-school science students probably know, nearly all of our natural gem minerals are crystallized, and usually fairly well so; that is, the crystals used for gems are either nearly perfect in crystallization or at least portions of them are clear and nearly free from flaws. Jumbled masses of tiny crystals will not yield clear transparent material such as is necessary for most of our fine precious stones.

The necessity of thus getting the artificial material into clear, well-crystallized pieces of sufficient size to make worthwhile cut stones more than any other factor made difficulty for the early experimenters in the production of "man-made" gems. The knowledge of the true chemical composition of the sought-for gem was, of course, a first essential, but it had been known for many years that diamonds were crystallized carbon and that rubies and sapphires were composed mainly of the oxide of aluminum before any one succeeded in getting artificially even tiny crystals of these substances.

It may be said at once that no considerable progress has been made as yet in the production, by artificial means, of any diamonds of large enough size to have any commercial interest. It may even be said that, since the

* Illustrations for Figures 5 through 12 were taken from "Die kunstlichen Edelsteine" by Univ.-Dozent Dr. Hermann Michel, and are reproduced herewith by courtesy of the publishers, Wilhelm Diebener, G.m.b.H., Talstrasse 2, Leipzig, Germany.

The color cuts used for the illustrations opposite page 1024 were obtained through the courtesy of Mr. Philip Fried of L. Heller & Son, Inc., New York City.

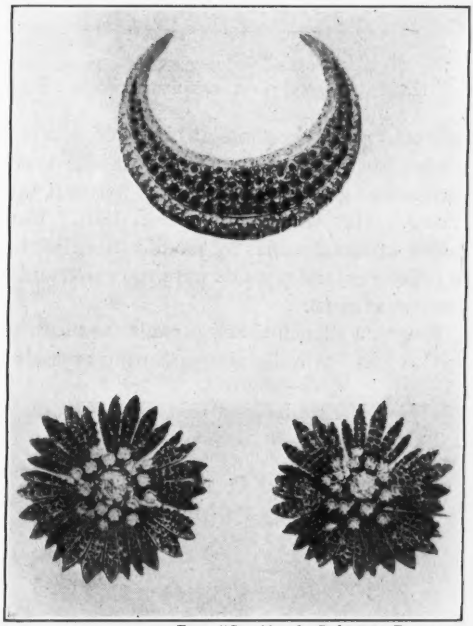
very thorough experiments of Sir Charles Parsons, the prospect for the making of diamonds of commercial size seems more dubious than ever. Those readers who may wish to become better acquainted with such success as has been had in the production of artificial diamonds will do well to seek reprints of "The Genesis of the Diamond" (*1*).

Passing on to consider those gems which have been successfully reproduced by man we find that the only commercial successes have been had with the sapphires and with the spinels. As was said above, the sapphires (and also rubies) of nature consist mainly of alumina, Al_2O_3, associated with traces of other metallic oxides. It is the latter substances which, in some way that is not as yet fully understood, determine the color of the stones. As long ago as the middle of the seventeenth century we find that, among the East Indians, there was some understanding of this similarity of stones of widely different color; for, in an old French copy of the travels of Tavernier, the great French gem buyer of that period, who journeyed six times to India and the East to trade in precious stones, we find a passage which may be translated as follows: "They call all other colored stones rubies in that country and they distinguish them only by their color. Thus, in the language of Pegu, the sapphire is a blue ruby, the amethyst is a violet ruby, the topaz a yellow ruby, and so on with the other stones." Tavernier goes on to say that they have some colorless "rubies" in the mines and that the natives call them "ripening rubies," having the belief that they will some day get ripe and be red. Thus we see that in the gem lore of that day, while there was much of error, there was some wisdom also, for today mineralogists call the oxide of aluminum gems *sapphires*, the ruby being a red sapphire, the others blue, yellow, white sapphires, etc.

This chemical similarity is dwelt upon because nearly all of the so-called "synthetic" gems of commerce are sapphires of one color or another, the only exceptions today being the magnesium aluminates, or "spinels," as the natural stones of this composition are called. Probably the chief reason that the early experimenters, as well as the later and more successful ones, worked with alumina is that the value of the fine ruby in the world's markets tempted them to reproduce it. There is little incentive to prepare the semi-precious stones artificially. They are too abundant in nature or of too low a price.

Glancing briefly over the early attempts to make rubies we are struck with the ingenuity of the experimenters in their efforts to make alumina crystallize. If we review our knowledge of the various ways and means of getting pure substances to crystallize we note that, in every instance, we must get the substance into such a condition that its particles may be free to move to their proper destinations in building up the geometrical space lattice that is the crystal. As we work in our high-school laboratories we sometimes cause alum, or blue vitriol, to crystallize and we use water as the

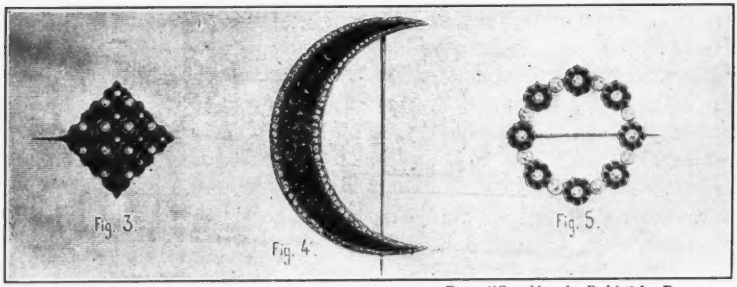
solvent to loosen up the particles and permit them to take again the form of crystals. This method (solution) was frequently resorted to by the early workers. They used substances such as borax or boric acid which melted before the alumina did and thus acted as solvents of the latter and, on cooling the melt, the alumina crystallized out from the saturated solution just as alum does from a hot saturated solution under similar circumstances. The crystals thus obtained by the seekers of rubies were, however, always very tiny and always in thin flat hexagonal plates, which form was unsuitable for cutting and polishing by the lapidaries. However, they were genuine rubies, for the fine red color was obtained by adding traces of chromium compounds which imparted the color to the whole crystal. One of the earliest workers to get such artificial rubies was the French chemist, Gaudin, who, in 1837, got both red and blue crystals of alumina. Gaudin used the oxy-hydrogen blowpipe to get the necessary heat to melt his solvent material and to dissolve the alumina. His materials were alum and potassium sulfate with a trace of potassium dichromate.



From "Synthèse du Rubis" by Fremy

FIGURE 1.—JEWELS SET WITH UNCUT RUBIES MADE BY FREMY

Other workers made use of another plan to get their rubies. They put together two materials which by a double decomposition with each other, under suitable conditions, would produce the desired product, so that it could crystallize. Thus, in 1850 de Senarment is said to have produced tiny ruby crystals by allowing chloride of aluminum to react with water while sealed up in a strong tube and heated to 350°C. What we have learned to call an "hydrolysis" probably took place and aluminum oxide crystals formed as the tube cooled off, leaving a hydrochloric acid solution. Other experimenters varied the first method by boiling off the melted solvent, much as sea water dries up in hollows of

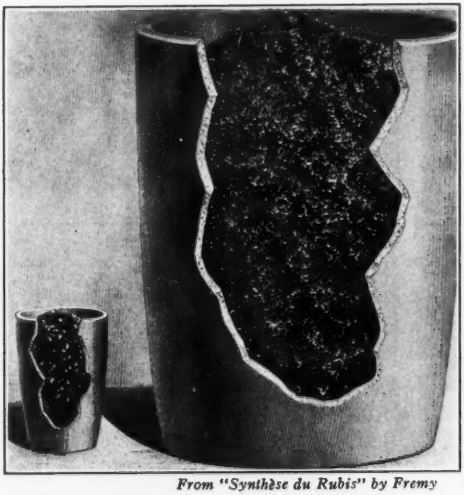


From "Synthèse du Rubis" by Fremy

FIGURE 2.—JEWELS SET WITH RUBIES MADE BY FREMY
The central jewel is set with uncut rubies, the other two with rose-cut rubies.

the rocks along the shore at high tide, leaving crystals of common salt behind. Ebelman was one who did this type of thing, using borax as his solvent and getting his crucible so hot that the borax was completely volatilized. This work was done in 1851. Various other experimenters obtained artificial rubies by modifications of these two general methods, but in every case the crystals were too small and too thin to be of any practical interest as gems.

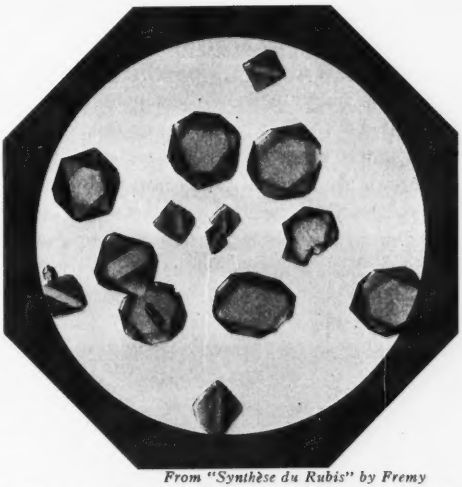
Fremy, a French chemist, came the nearest to succeeding of all the early workers and actually got some ruby crystals which were cut and polished and mounted in jewelry. His report of his experiment was published in 1891. His largest ones weighed only about a third of a carat when uncut and about a sixth of a carat when polished so they were of only very trifling value as precious stones. (Figures 1 and 2.) His final work was done with the assistance of a young man named Verneuil and, in his splendid monograph, "Synthèse du Rubis," he has this to say of his young assistant: "During my long research, my young collaborator.....



From "Synthèse du Rubis" by Fremy

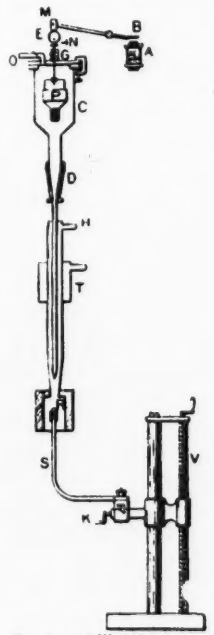
FIGURE 3.—CRUCIBLES USED BY FREMY TO MAKE RUBIES
Laboratory and industrial furnace sizes.

has given proof of great perseverance and of a very remarkable spirit of observation." This passage is quoted because it was this same Verneuil, who somewhat later, after the death of his old master, succeeded in finding a way to make rubies and sapphires of large size and great perfection; and, as a result of his labors, millions of carats of synthetic stones have since been made and marketed.



From "Synthèse du Rubis" by Fremy

FIGURE 4.—SOME OF THE ARTIFICIAL RUBIES MADE BY FREMY
Magnified about 50 diameters.



Courtesy of Wilhelm Diebener G.m.b.H., Leipzig

FIGURE 5.—DIAGRAM OF BLOWPIPE FURNACE FOR MAKING RUBIES

Fremy's final method, by means of which he got rubies large enough to cut (Figures 3 and 4), was as follows (literally translated from his original paper): "These rubies were produced in a crucible of refractory earth by causing to react, at a very high temperature, a mixture of alumina, more or less 'potassée' (mixed with small amounts of potassium carbonate), of fluoride of barium, and of bichromate of potassium." Fremy himself was in doubt as to just what reactions took place in his crucible. He found that it was absolutely necessary to allow moist air to have access to his material which, of course, suggests that hydrolysis played an important part in the reactions. He infers that the rubies resulted from one or the other of the two following series of reactions: (1) the formation of alkaline aluminate, followed by its decomposition by hydrofluoric acid gas (which resulted from the hydrolysis of his barium fluoride at a high temperature under the influence of water vapor), thus producing crystalline alumina and volatilizing the alkaline fluoride; or (2) a preliminary formation of fluoride of aluminum

at about 1500°C. followed by its hydrolysis, with the production of crystallized alumina and hydrofluoric acid.

In his earlier and less successful experiments Fremy made use of a reaction which might perhaps be repeated by those of our readers who have been anxious to make artificial rubies. He says, "We obtained the rubies by causing to react, at a bright red heat, in a crucible of refractory earth, a mixture of alumina, of potassium bichromate, and of minium (red lead)." He explains the reactions as follows: "There is produced, in this reaction, lead aluminate, which is then decomposed by the silica of the crucible, forming fusible silicate of lead and crystallized rubies." All very simple. Fremy even gives us simple directions when he says: "To obtain the rubies by this method, we heated, during several hours, a mixture of equal parts of alumina and of minium mingled with three per cent of bichromate of potassium." He goes on to say that when the mixture is heated "regularly," "we find in the crucible, after its cooling, two layers, the lower is vitreous and formed principally of lead silicate; the upper layer is crystallized and filled with rubies in a matrix of lead silicate."

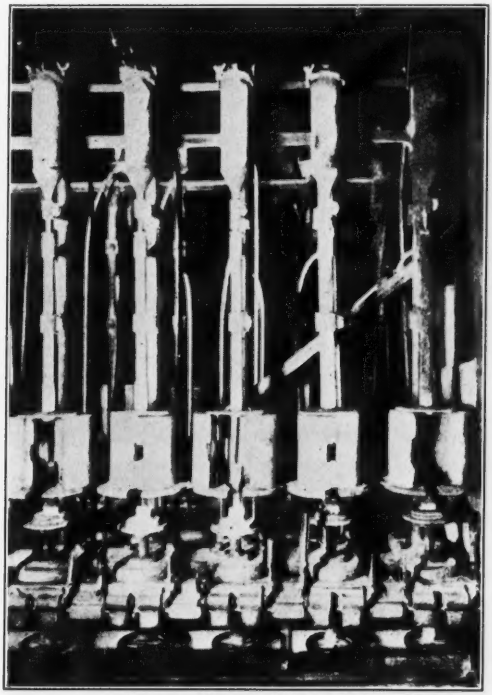
Courtesy of Wilhelm Diebener G.m.b.H., Leipzig

FIGURE 6.—"BOULES" (*French*) OR "SCHMELTZTROPFEN" (*German*) ON THEIR SUPPORTS

Those who try out this method must not expect to get any but very tiny and very thin crystals of ruby, for Fremy himself never got any thick ones in this way, although he resorted to industrial furnaces and got at times several kilograms of ruby to the crucible. Some of these had very considerable "spread" but they were always very thin hexagonal plates. It was a matter of "crystal habit" and it was only when he resorted to his other method, some years later, that he got the rubies in rhombohedral form and sufficiently thick to cut.

Before going on to tell something of Verneuil's method we should look back many years to consider an experiment made by Dr. E. D. Clarke in 1819. He was working with the newly discovered oxy-hydrogen blowpipe and while trying its power to melt very refractory things he says: "Two rubies were placed upon charcoal and exposed to the flame of the gas blow-

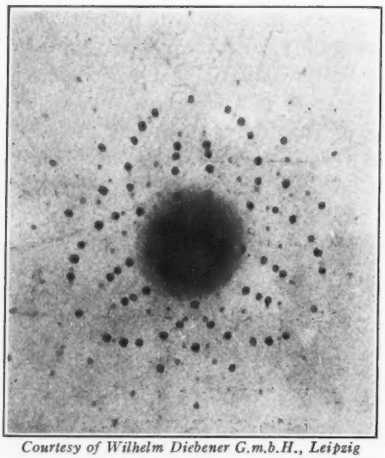
pipe.....after suffering it to become cold.....the two rubies were melted into one bead." Here was where Dr. Clarke lost an opportunity to become famous, for he did not discover that the material had recrystallized in one crystal, but evidently assumed that it had become a "glass," as borax does on being heated in the Bunsen flame (the phenomenon observed when making "borax beads" for testing certain metallic oxides in qualitative analysis). Skipping on to about 1885 we find that a later experimenter, probably in Geneva, Switzerland, learned of the possibility of melting several pieces of ruby into one piece and was alert enough to detect the true crystal condition of the bigger new piece. As a result, a considerable number of really "reconstructed" rubies came on the market and were sold, probably in most cases without the knowledge of the buyer that there was anything artificial about their origin. They were, of course, genuine as to substance, properties, crystal form, etc., and so were not readily detected as synthetic by those in the trade who handled them. In most cases, however, there were round gas bubbles in these rubies as a result of the use of the blowpipe; and nature's rubies *never* have round cavities in them. Cavities sometimes occur in natural rubies but they are always angular and tend to resemble the crystal itself in their form, being "negative" crystals or vacancies in the lattice of the crystal. The color of these "reconstructed" rubies was seldom like that of natural rubies of the better sort and eventually the facts in the case came out and "the game was up."



Courtesy of Wilhelm Diebener G.m.b.H., Leipzig

FIGURE 7.—SERIES OF SYNTHETIC RUBY FURNACES

Shortly after this Verneuil hit upon his new method and began preparing,

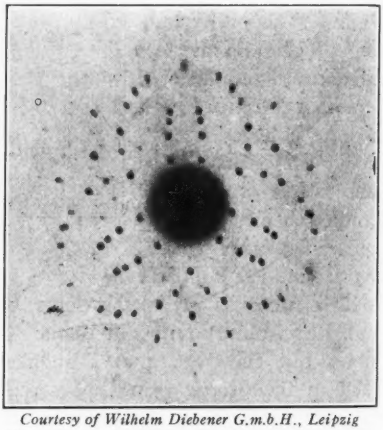


Courtesy of Wilhelm Diebener G.m.b.H., Leipzig

FIGURE 8.—LAUE DIAGRAM (X-RAY PICTURE) OF SYNTHETIC RUBY CRYSTAL STRUCTURE

Taken perpendicular to the base of the hexagonal crystal.

first rubies and later sapphires of various colors (*2*). His very ingenious method consists in melting prepared alumina (mixed with one or two per cent of a suitable colorant such as chromium oxide for the ruby color) by causing the powder to be melted in order to pass *with one of the gases through the flame* of the blowpipe, then to crystallize on a refractory support below (for the flame is directed vertically downward) (Figure 5). What happens is this: the first material to crystallize determines the orientation of the crystal, by forming a minute "seed" crystal, and thereafter, if the conduct of the experiment is skilful, all the molten material that arrives from above lines up with the space lattice of the seed crystal and the finished mass is a single crystal, although it usually resembles an inverted pear and appears upon superficial study to be a glassy mass. (Figures 6 and 7.) We have somewhat the same effect that we have in an icicle, which is a crystal of water that grows *down* rather than *up*. The icicle, like the ruby "boule" (as the French call it), is transparent, because it is a single crystal, not a mass of many smaller crystals. Verneuil placed his powdered raw material in a small "hopper" equipped with a mechanical tapper to sift the material down into the oxygen gas in a uniform and controllable manner. (See Figure 5.) Considerable skill is required to properly adjust the gas pressure and the proportion of fuel gas to oxygen, and for the placement and manipulation of the support,



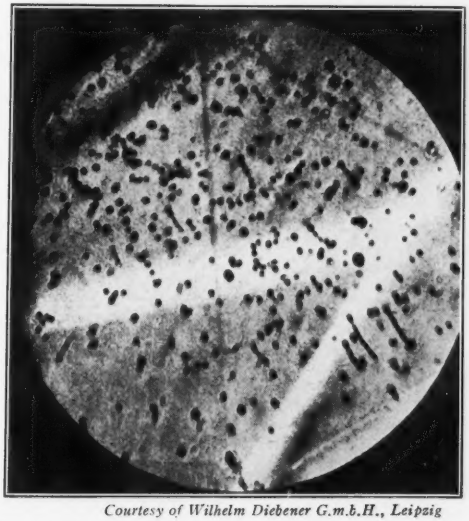
Courtesy of Wilhelm Diebener G.m.b.H., Leipzig

FIGURE 9.—LAUE DIAGRAM OF A NATURAL RUBY

Taken in the same direction as that of Figure 8.

so as to start the first crystal and to keep the boule growing regularly and perfectly; but such skill has been acquired by so many workers in several European countries that the finished products can now be had very cheaply.

Synthetic stones are cut and polished in the same manner as natural stones and have the same properties, so that it is not possible to distinguish them from natural rubies and sapphires by the usual tests, which serve to tell the various kinds of natural stones from each other. The color is sometimes very fine, the hardness is correct, the specific gravity closely similar to that of the natural stones, even the refractive index and the double refraction are correct and, to go the limit, an X-ray picture (Laue diagram) of the synthetic material is identical with that of the natural stone. (Figures 8 and 9.)

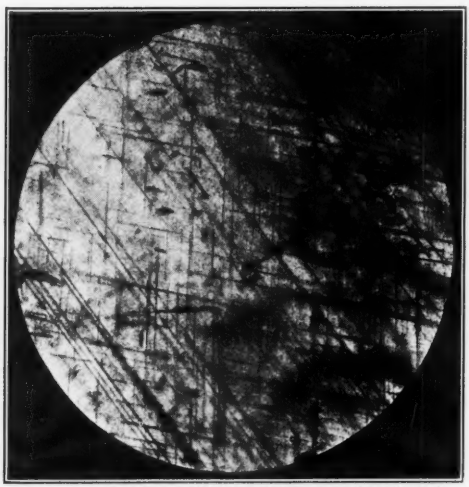


Courtesy of Wilhelm Diebener G.m.b.H., Leipzig

FIGURE 10.—GAS BUBBLES (HIGHLY MAGNIFIED) IN A SYNTHETIC STONE

How then may one tell whether or not he has a natural ruby or sapphire? This is not as difficult as it might seem, for the micro-structure of the artificial stones is seldom or never perfect, and the structure of the natural stones also, in most cases, shows faults under a good magnifier. Fortunately, the two types of structure or rather of failure in structure are quite dissimilar. Like the "reconstructed" ruby, the synthetic one frequently has gas bubbles in it and these bubbles are always *round* or *rounding*, while the natural stones have *angular* cavities when any are present. (Figure 10.) Moreover most natural rubies show at least traces of fine, *straight*, parallel, silky lines within them and these lines cross other sets of similar lines at sixty-degree angles, there being three such sets of lines, since the ruby (and sapphire) belongs to the hexagonal system of crystals. (Figure 11.) These lines may be seen best by allowing a strong light to cross the stone while the observer looks at right angles to the line of advance of the light with a good magnifier. In this manner an effect resembling the "Tyndall effect" in the ultramicroscope is obtained, and ex-

tremely tiny structural defects become apparent. Gem dealers call the condition that we have been describing "silk" because of the resemblance to the parallel lining of a fine silk fabric. Synthetic stones have never been observed to have this texture. On the contrary they usually have, instead, a series of *curved* parallel lines which may be seen by similar tactics to those above described. (Figure 12.) It may be necessary in some cases to turn the cut stone very slowly from one position to another until a flashing glimpse of the internal structure is caught; but in some position, by a suitable light, one can usually detect this structural defect. It is perhaps due to extremely slight variations in color in successive layers as laid down on the usually *rounding* head of the growing boule, thus causing the curving, nearly parallel, striae that betray the artificial origin of the stone.



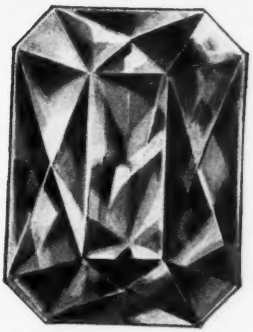
Courtesy of Wilhelm Diebener G.m.b.H., Leipzig

FIGURE 11.—THE ORIENTATION OF INCLUSIONS OF RUTILE IN A NATURAL BURMA RUBY

Structure such as this is never seen in synthetic stones.

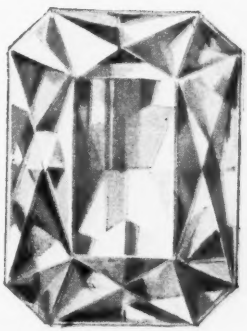
The usual cutting of the synthetics is done so cheaply that the cutter cannot afford to do the very careful and expert work that is applied to the costly natural ruby. This lack of fine finish betrays the commercial synthetics to one conversant with lapidary work. When, however, an attempt to deceive is involved, the finest of lapidary work may be given a synthetic product and considerable skill will then be required to determine whether or not a given specimen is natural or artificial. Fortunately, however, there is very little reason to believe that there is anything of that sort going on in legitimate channels of trade. A few cases have come to our attention in which native Eastern lapidaries have skilfully cut synthetic rubies in native fashion and disposed of them to "steamboat gentlemens," as they designate tourists.

Recently [(*3*) and (*4*)] a new means of distinguishing synthetic gems from natural ones has been developed by the laboratories of the General Electric Co. at Lynn, Massachusetts. Using the Coolidge type of tube and exposing the stones to be tested to the powerful cathode rays that are shot



SAPPHIRE

SPINEL



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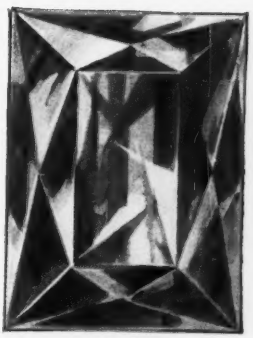

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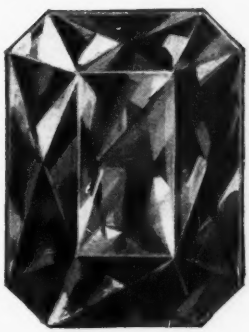

SAPPHIRE

SPINEL

SYNTHETIC GEMS

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out through the very thin metallic window of the tube, it is found that there are differences in the color of the fluorescence excited in the stones by the fast-flying electrons from the tube. By testing synthetic stones from different factories it is even found that it is possible to distinguish between them, probably because of slight differences in the quantity of impurity introduced to give the stone the desired color. Natural sapphires from different mines can also be distinguished from each other, as well as from synthetics. There is, moreover, in some cases a subsequent phosphorescence after the tube ceases to act, which may be used to still further distinguish between the synthetic and the natural stones. Of course such modern equipment is not available in most cases where the question of the character of gems is raised, and it is still necessary to rely on an expert eye, provided with a good magnifier, for the desired verdict.

Courtesy of Wilhelm Diebener G.m.b.H., Leipzig

FIGURE 12.—CURVED PARALLEL STRIAE IN SYNTHETIC STONES

These are never seen in natural stones.

Among the principal colors now to be had in synthetic stones are various shades of ruby red and of pink, fine sapphire blue, and paler blue (resembling the Ceylon type of sapphire), golden yellow, a pinkish orange (like the natural sapphire called padparadsha by the East Indians), the pure white sapphire (which is usually cut "brilliant" like the diamond), a somber green (much like some Ceylon tourmalines), a golden green, and a peculiar double-colored variety, which is sold as "synthetic Alexandrite" and which has a bluish green color by bright daylight but an amethystine pink by artificial light. This latter result is probably obtained by the use of two colorants, one of which produces a color that requires short-wave length light, abundant in bright daylight, to pass through it, while the other color is best seen when the relatively longer wave length light of artificial origin passes through it. The natural Alexandrite is a peculiar chrysoberyl and is of totally different character, chemically and physically, from sapphire. The several producing companies have trade-marked names for

certain colors of synthetic stones, some being borrowed from the names of natural stones and others being purely fanciful.

Among the spinels which have come on the market we find principally the fine sky-blue variety that simulates the artificially colored "blue" zircon and the lighter aquamarine-blue spinel which is used as a substitute for aquamarine or blue beryl; and, recently, considerable numbers of colorless synthetic spinels which simulate the white zircon and are used as substitutes for diamond. While very lively in their white brilliancy they lack sufficient dispersion to give the sought-for rainbow colors, so vivid in the case of a fine blue-white diamond, and the surface luster of the white spinel is also unlike the adamantine luster of the diamond. Various other colors in spinel are produced in Europe, an Alexandrite-like variety being one of them and a fairly deep blue variety said to owe its color to cobalt, another. The color of the latter is not equal to that of the synthetic sapphire and reminds one of the piercing blue of cobalt glass.

In conclusion we may say that man has now equaled all but perhaps the very rarest of Nature's sapphires and rubies and greatly excelled the general run of the natural stones in color and perfection, as well as in size. In quantity, also, we have outrun Nature so that now "the maiden in her dairy" as well as "the queen upon her throne" may have numerous, fine, large gems, for the present-day cost of the synthetic stones is only nominal. Indeed they are delivered to the consumer, with the tariff paid and with all profits, for less than the American lapidary can afford to cut the rough material under our higher standards of wages. We fancy we hear the inquiry, "Have not the natural gems been hurt in price by the invasion of the synthetics into the gem trade?" Probably not in the least. Indeed sapphires have been much higher in price since the coming of the synthetic sapphire than ever before. This is all a matter of "psyrology" as "Andy" would say, or as an old man said to a young one once, "Young fellow, as the Bible says, as a woman thinketh so is she, and don't you forget it!" Thus it is, as men think, so is the price established, and no man thinks he wants to pay very much for anything that can be had in quantity by everybody, with small effort. On the other hand, the exceedingly rare Burma ruby of fine quality and of appreciable size will ever command competitive bidding from numerous wealthy seekers for that which is at once rare and rarely beautiful.

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LIQUID AIR

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Suggestions are given for the storage and handling of liquid air and liquid oxygen. Manipulations are described for the performance of a number of rather striking experiments which are designed to bring out the properties of liquid air and especially to demonstrate its low temperature. This material is then used to show the effect of low temperature on the properties of familiar substances. The preparation of liquid oxygen is described as well as experiments to illustrate its power as a supporter of combustion. Some of these latter experiments are particularly brilliant.

. . . . . .

The many letters of inquiry that have come to the editor of the JOURNAL OF CHEMICAL EDUCATION and to the author indicate some real interest in experimental demonstrations with liquid air. Therefore, we shall attempt to describe some which we have found to be safe, sure, and easy to perform, as well as more or less spectacular.

Supplies of liquid air may usually be secured by making arrangements in advance with the plants engaged in preparing oxygen commercially from the air, such as the Linde or Air Reduction Plants. These companies are located in nearly all of the larger cities. As a rule the liquid obtained from such sources will be fairly pure oxygen instead of liquid air, but it will be suitable for most of the demonstrations.

Liquid air or liquid oxygen must be shipped and stored in vacuum-jacketed vessels; suitable glass vacuum vessels holding about six pints may be obtained from the Icy Hot Division of the American Thermos Bottle Company, Norwich, Connecticut. Since these have glass fillers they must be handled with care. It is best to order the fillers directly from the company and explain that they are for use with liquid air because then they furnish a superior quality especially adapted to the purpose. Larger quantities of the air are best shipped and stored in large metal Dewars which may often be rented from the Oxygen Company. Of course, liquid air or liquid oxygen must never be corked tightly, because no matter how efficient the vacuum jacket may be, heat will leak in and the temperature will rise unless free evaporation is permitted; and as the temperature rises the pressure will increase until either the stopper is driven out or the vessel is ruptured.

It is always risky to pour liquid air from a glass Dewar (as vacuum-jacketed vessels are often called) because the sudden cooling of the lip where the seal between the inner and outer parts of the filler is made is very likely to cause the filler to collapse. On this account the air should be pumped out of the container with a device such as is shown in the accompanying sketch (Figure 1). This is the same in principle as the familiar wash bottle with the addition of a stopcock which is opened

when it is desired to stop the flow of the liquid air and an atomizer bulb to furnish the air pressure required to force out the liquid. If liquid air is to be transferred to another Dewar which is at room temperature, the latter should be cooled as slowly and as evenly as possible. A good way to do this is to take the Dewar in the left hand and, while giving it a swirling motion, to pump in a little liquid air, keeping the Dewar in constant motion so as to cause the liquid to travel over as much of the inner surface as possible. When the first lot of liquid air is nearly gone, add a little more, swirling as before until the Dewar is cooled down to the point where the liquid air passes out of the spheroidal state and wets the glass. Then the liquid may be added more rapidly, but it is well to keep the Dewar agitated while it is being filled. The necessity for these precautions will be appreciated when it is realized that the glass is suddenly cooled from $+25°C.$ to $-195°C.$ No precaution need be taken in adding liquid air to ordinary pyrex flasks or beakers. They practically never break, nor does the experimenter need any protection for his hands if he is always careful to pick up the beakers, etc., by their tops.

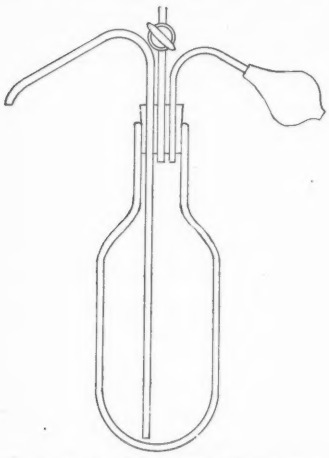


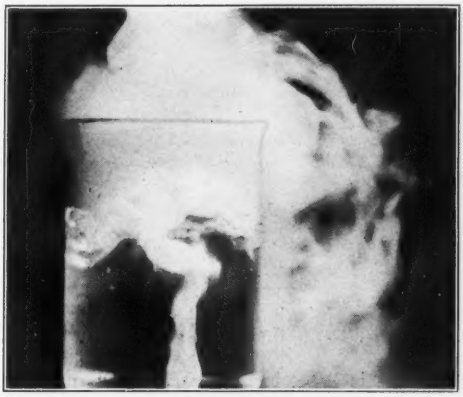
FIGURE 1.—CONTAINER USED FOR PUMPING OUT LIQUID AIR

There is no danger to the experimenter from splashing liquid air because even if it apparently strikes the hand or face it will not really touch the skin. The explanation for this is to be found in the fact that liquid air in apparent contact with anything at ordinary temperatures assumes the so-called spheroidal state, that is, the air is caused to evaporate so rapidly that the rush of gaseous air keeps the liquid from actually touching the object. So one may, with perfect safety, pour the liquid over the hand, or plunge the latter for a moment into the liquid air. One can demonstrate that the hand has been below the surface of the liquid air by reaching down into the liquid with the fingers of one hand, pressing their tips lightly against the side of the beaker; then by rapidly withdrawing the hand enough liquid air is swept out and falls on the table for every one in the room to see.

Most of the experiments with liquid air fall naturally into two classes: first, those that depend upon the property that even when boiling, liquid air has a very low temperature, and second, that upon partial evaporation it furnishes a source of nearly pure oxygen.

General Experiments

Experiment 1.—An experiment to show qualitatively the relation between the density of liquid air and water and its change as the liquid boils may be easily performed by filling a 500-cc. beaker two-thirds full of water and then pouring about 50 cc. of liquid air upon the water. At first the liquid air floats, showing a density less than 1, but in a short time globules of the liquid air begin to take excursions toward the bottom of the beaker, showing that the liquid has become more dense than water. At this stage a test of the gas escaping from the liquid in the well-known way, using a splinter with a glowing spark on the end, will show that it is oxygen of high concentration. It can now be pointed out that the experiment shows that since liquid oxygen (density 1.14) is more dense than water and liquid air less dense, liquid nitrogen (density 0.808) must be considerably less dense than water.



LIQUID OXYGEN SINKING IN WATER

The experiment also shows that nitrogen (b. p. −195.8°C.) boils more easily than oxygen (b. p. −183°C.) and passes off first when a mixture of the two is allowed to boil. Attention may be called to the fact that this is the basis of the most commonly used method for the commercial preparation of oxygen, that is, the liquefaction and fractional distillation of air.

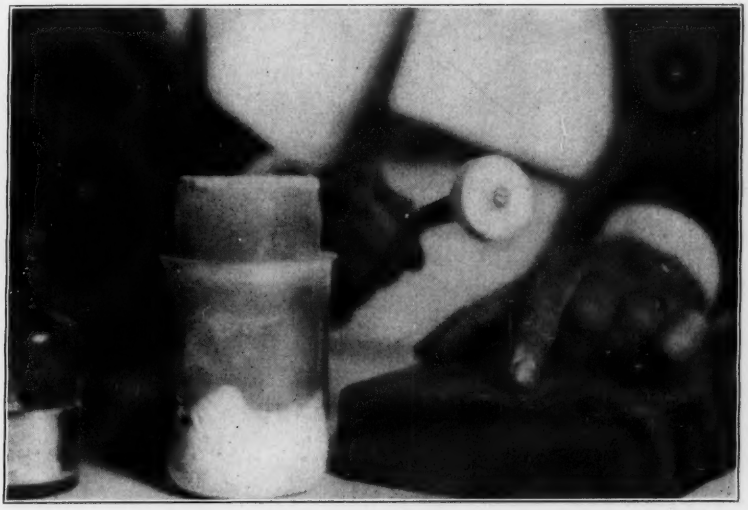
Of course, if only liquid oxygen is available for this experiment the liquid will be more dense than water from the start, and the experiment will lose most of its point. The last small globule of oxygen commonly floats on top of the water in a little boat of ice which may be removed with the hand, letting the liquid oxygen drop back into the beaker to form another yet smaller boat. The audience is surprised at the small quantity of ice formed and must be told that while the boiling air has a very low temperature its total refrigerating power, the heat of vaporization plus the heat taken up in warming the gaseous air to ordinary temperatures, is only about as great as that of the melting of an equal weight of ice.

Experiment 2.—The audience looks at boiling liquid air, surrounded as it is by a cloud of frost and fog, and thinks that it is hot, because water

CRUSHING THE FROZEN FLOWERS

when it is "steamy" is hot. So a number of experiments are in order to show that when liquid air is hot enough to boil (−195°C. to −183°C.) it is still very cold in comparison with ordinary temperatures. For the first of these one may use the freezing of flowers. If available, use a half-pint unsilvered glass "food jar" type of Dewar about half-filled with liquid air. Any flowers may be used, but those with thick fleshy petals take too long to freeze to work well. Carnations are best. Pick up a flower and show that it may be pinched and rolled between the fingers without harm and then immerse in the liquid air for a few seconds, just long enough for it to become wet with the liquid; then remove the flower from the jar and crush it between the fingers once more. The flower falls to pieces. Of course, it does not take an extremely low temperature to freeze a flower, but the rapidity of freezing never fails to impress the audience.

Experiment 3. Freeze Cranberries.—Place the berries in a beaker and pump the air over them, ocassionally giving the beaker a shake. Presently the cranberries become frozen and rattle against the glass like marbles. Continue to pump the air over the cranberries until you find



DRIVING A NAIL WITH A MERCURY HAMMER

by pinching them that they are frozen hard. Then cover the beaker with a watch glass and drain off the remaining liquid. This may be put in a previously cooled Dewar as a part of the supply of liquid oxygen for combustion experiments. Throw the cranberries by handfuls out over the audience. They will scramble for the berries and be much impressed by their low temperatures.

Experiment 4. Freeze Mercury.—For this experiment we usually make a mercury hammer, using as a mold for the head as large a round pasteboard box, such as druggists use for dispensing pills, as will easily slip into a wide-mouth Dewar. This box we fasten to the end of a stick (the handle) about a half-inch in diameter by a small screw and washer to increase the bearing surface. It will be of advantage to have the washer larger in diameter than the end of the stick to prevent the mercury head from flying off the handle. With the Dewar about half or two-thirds filled with liquid air, fill the pill box with mercury and lower it below the surface of the liquid air. When the liquid air has ceased its violent boiling the mercury may be withdrawn from the Dewar and tested by pressure to see if it is thoroughly frozen. If so, the pasteboard box may be peeled off from the frozen mercury and the latter exhibited to the audience. A tack may be driven into a piece of soft wood with this mercury hammer but not a small-headed nail into hard wood because, as you can demonstrate to the audience, frozen mercury is very much like lead and may be easily cut with a knife.

FROZEN ALCOHOL

This frozen mercury may be safely handled with the bare hands because, although its temperature is at least 40°C. below zero, it is a poor conductor of heat. That it is cold may be demonstrated to the audience by plunging the hammer into a beaker of water when the frozen mercury will be almost instantly replaced by a block of ice. While the mercury is freezing it would be well to remind your hearers that since a substance cannot be frozen at any temperature higher than its freezing point, and the freezing point of mercury is −40°C., success in this experiment shows that boiling liquid air must be at least 40° below zero.

Experiment 5. Freeze Alcohol.—For this experiment place 20 to 25 cc. of alcohol in a 100-cc. beaker; pour in a little more than an equal volume of liquid air and stir with a glass rod. The alcohol freezes very quickly and if just the right amount of air has been added, enough unfrozen, but very viscous, liquid will be left so that a lump of frozen and half-frozen alcohol will cling to the rod and may be withdrawn from the beaker and exhibited to the audience. If too much air has been used the alcohol will be frozen to a mass of dry fragments which will not cling to the rod until they have begun to melt. Since alcohol freezes at −117.3°C., success in this experiment means that liquid air must have a still lower temperature. Care must be taken to keep a flame away from the mixture of air and alcohol and also to keep the half-frozen alcohol out of contact with the hand because it, unlike liquid air, clings to the skin and instantly produces such severe freezes that blisters and other painful effects similar

to those of deep burns will follow. At this point the author usually explains this fact and demonstrates the harmlessness of liquid air as indicated above. In addition, he usually takes some of the liquid air into his mouth, exhaling a great cloud of fog and then by dropping the chin, lets the liquid air run out on the table. There seems to be no danger of freezing one's tongue, provided the liquid air is perfectly clear and free from solids.

HOLDING LIQUID AIR IN THE MOUTH

One should be careful not to let the beaker containing the liquid air touch the lips or the tongue, and also not to swallow much, if any, of the liquid air for the simple reason that when it evaporates it increases eight hundred times in volume. In case too much liquid air is accidentally swallowed, tickling the palate brings prompt relief.

Having shown in experiments 2, 3, 4, and 5 that boiling liquid air is relatively cold, the influence of this low temperature upon the properties of some familiar substances may be shown as follows.

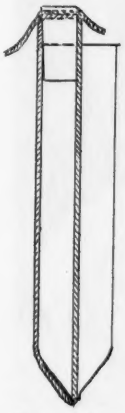
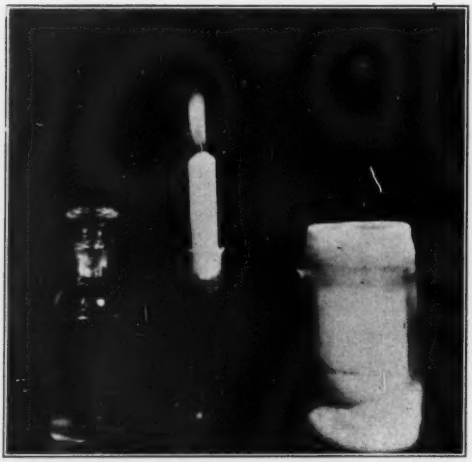


FIGURE 2.—MOLD FOR KEROSENE CANDLE

Experiment 6. Make a Candle of Kerosene.—Prepare a candle mold by drawing down before the blowpipe a small test tube to form a conical end like that of a candle, and cut it off so as to leave a small hole through which a cotton string may be threaded. This string is to serve as a wick. It is held in the center of the open end of the mold by a cork, split in half lengthwise. A slit is cut in the top of the cork to hold the string in place. The other end of the string may be brought up outside of the test tube and fastened in the same slit in the cork (Figure 2). The mold is half-filled with kerosene, inserted into liquid air, and kept there until the kerosene is just frozen which may be determined by withdrawing the mold from time to time and tipping it to see if the kerosene will flow. If allowed to become too cold the kerosene would be so brittle



KEROSENE CANDLE

that the candle would crumble to pieces when withdrawn. To remove the candle from the mold cut off the string at the conical tip, plunge the mold for an instant into water, and then draw out the candle by the wick. Insert in a small candlestick and light the candle. It will burn well, but naturally, since it is kerosene, it has a smoky flame. There is a tendency for some of the kerosene to leak out before it freezes and, therefore, the air that has been used for this experiment should not be used in combustion experiments because of the highly explosive character of the liquid oxygen-hydrocarbon mixture.

Experiment 7. Effect of Low Temperature upon Rubber.—Place a small *hollow* rubber ball in a beaker of liquid air. Roll the ball around

BREAKING THE FROZEN RUBBER BALL

for a few moments with the fingers until it is thoroughly cooled and the sound of its contact with the beaker shows that it is hard. Then decant the air and hurl the ball to the floor or table. It will fly to pieces as though made of glass. If picked up immediately these pieces may be broken between the fingers but, after warming for a moment in the hands, they become as rubbery as ever.

Experiment 8.—The effect of low temperature on colors may be shown by placing red lead, sulfur, and copper sulfate in test tubes and cooling with liquid air. Reds tend to become yellowish; yellows, white; while blues are generally changed but little.

Experiment 9. Condensation of Gases.—If natural gas is available, it may be liquefied by passing the gas into a small distilling flask through a tube reaching nearly to the bottom, while the bulb is surrounded with liquid air. The flow of the gas should be so adjusted that while at ordinary temperatures a flame about four inches long will burn at the delivery tube of the bulb. Let the gas burn and immerse the bulb in liquid air. As soon as the air wets the flask, the flame will suddenly go out, showing the liquefaction of the methane. After a few cubic centimeters of liquid have collected, the gas may be cut off, and the bulb removed from the liquid air when, upon warming, the methane boils, and the escaping gas may be lighted.

Hydrogen chloride, hydrogen sulfide, and chlorine may be condensed in the same fashion, or more simply by running them into test tubes surrounded by liquid air. They are odorless solids at liquid-air temperatures.

Experiment 10. Adsorption of Gases.—Cocoanut charcoal or charcoal of similar adsorbing qualities may be used to produce a rather high vacuum in a very short time by the adsorption of the gases of the air. A simple way to show this is to select two glass tubes, each about a meter long, and a centimeter or so in inside diameter. Seal each tube at one end, and bend one over to make a side-arm about twelve to fifteen centimeters long. The end of the tube should be bent through about 135 degrees so that the arm makes an angle of about 45 degrees with the main part of the tube and so slopes downward when the tube is placed in vertical position with the open end downward. This side-arm should be filled with the adsorbent charcoal that has been previously dehydrated by heating. After the charcoal has been put in the side-arm, the tube should be placed in a vertical position with the open end below the surface of mercury in a dish. The other tube

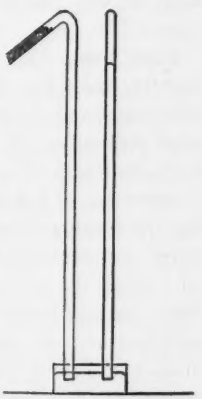


FIGURE 3.—ADSORPTION OF GASES

should be filled with mercury and inverted with its open end in the same dish of mercury as the charcoal tube. This will furnish a barometer with a Torricellian vacuum above the mercury (Figure 3). Now cool the charcoal in the side-arm of the other tube by surrounding it with liquid air in a Dewar. The gaseous air in the tube will be adsorbed, and a vacuum even better than that in the barometer tube will be quickly formed, as shown by the rise of the mercury in the tube containing the charcoal. At liquid-air temperatures all gases, except helium, neon, and hydrogen, are practically completely adsorbed, and appreciable quantities of hydrogen and neon are taken up.

Experiment 11.—That pressures will develop if an attempt is made to confine liquid air by corking it, may be shown by making a very strong test tube out of pyrex glass, about 30 cm. long and 1.5 to 2 cm. in diameter. Put six or eight cm. of liquid air in the bottom of this tube, wait until the boiling has quieted down, and then insert a well-rolled cork. In a few moments the cork will be driven out and across the room with a decided pop and force enough to be impressive.

Experiment 12.—This force exerted by expanding and evaporating liquid air may be utilized to drive a toy engine. For this, use a strong tube or a small, strong flask as the boiler, and connect this boiler with the steam engine by a small heavy-walled rubber tube. The exact manner of making this connection depends upon the construction of the engine, and must be left to the ingenuity of the experimenter. The liquid air cannot be placed directly in the boiler of the engine, because it will be evaporated more rapidly than the engine can take care of it. The sight of a steam engine running without any fire, with the boiler cold enough to "scale up" with frost, is striking, and seems to indicate possible industrial applications; but the over-all efficiency is very low, probably not more than 1% at best.

Experiment 13.—Some liquid air placed in a small coffee pot boils merrily, throwing off a great cloud of fog and frost, simulating the so-called steam of the tea-kettle, when held in the air, placed on the table, or, most striking of all, set on a block of ice. The ice is often so cooled that it cracks under the coffee pot.

After the air has boiled on the ice for a moment, the pot may be picked up, the coating of frost wiped from its bottom, and the flame of a Bunsen burner or alcohol lamp brought to bear directly upon the metal bottom. Of course, the air boils furiously, but right in the midst of the flame, a white coating forms anew on the pot. After a moment or two, the flame may be removed, and this coat, which consists of a mixture of solid carbon dioxide and frost, may be flaked off the bottom and demonstrated to the audience. The audience should be impressed with the fact that the presence in this coat of solid carbon dioxide, which cannot exist at a higher

LIQUID AIR BOILING ON ICE

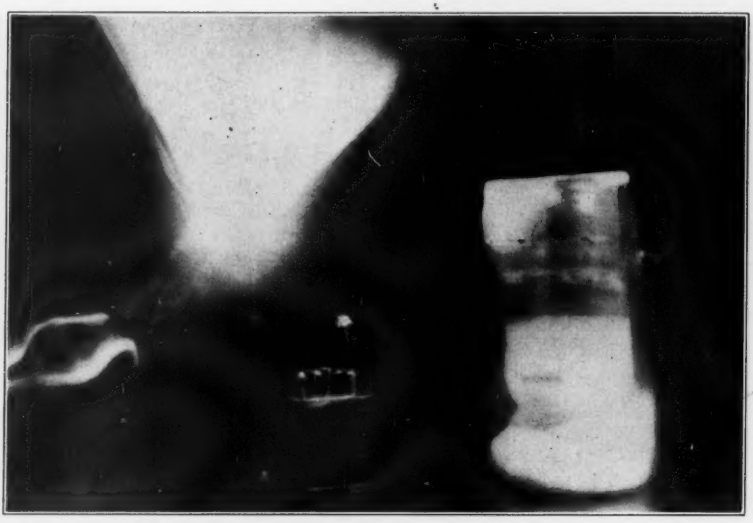
temperature than −78.5°C. at atmospheric pressure, shows that liquid air has produced a temperature of at least −78.5°C. in the middle of one of our very hot fires—a temperature low enough to freeze the products of combustion while still surrounded by the flame.

Experiment 14.—Wire solder may be coiled into the form of a helical spring, which when cooled to liquid-air temperatures will vibrate up and down while supporting a load of a hundred grams or so, but which will lose its elasticity and straighten out when it warms up to room temperature.

Experiment 15.—The effect of low temperatures in increasing the electrical conductance of a metal may be shown by taking a two-cell flashlight bulb and putting between it and two dry cells a coil of fine insulated copper wire of about 15 ohms' resistance. This added resistance will cut down the brilliancy of the lamp very decidedly. Now cool the copper coil in liquid air, and the little lamp lights up to nearly full power. Remove the liquid air, and as the coil warms up the lamp becomes duller again.

Combustion Experiments

A number of spectacular experiments may be performed with liquid oxygen as a supporter of combustion. If the liquid has been obtained from the oxygen companies, it will probably be ready for use in these experiments without any additional preparation. If liquid air is the starting material, a liter or more of it should be drawn off into a beaker twenty



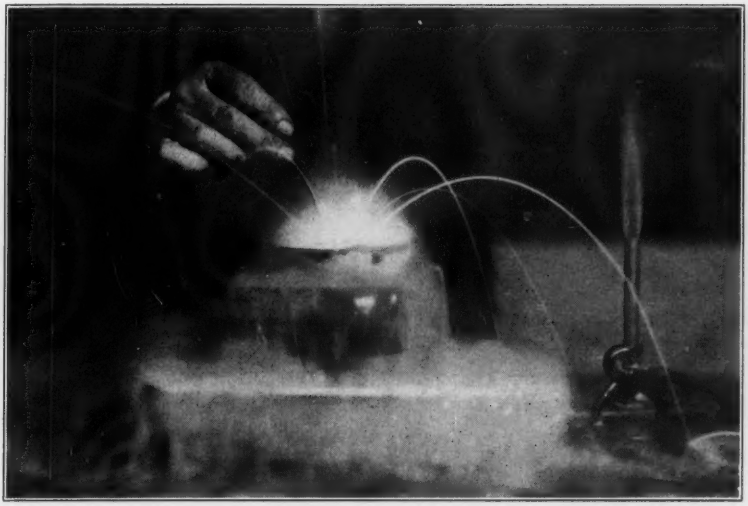
BURNING CIGAR SATURATED WITH LIQUID OXYGEN

minutes or so before it is to be used, and allowed to evaporate until one-half to two-thirds has escaped, or until tests with a glowing splinter show that the escaping gas is good oxygen. The remaining liquid should then be transferred to a Dewar for storage until needed. At this time it is well to place a cigar, prepared as for smoking by clipping off the tip, into the liquid oxygen, in order that it may become well saturated with oxygen.

Experiment 16.—Place about 25 cc. of liquid oxygen in a small beaker and plunge a splint with a glowing spark on the end beneath the surface of the liquid oxygen. Of course, it burns brilliantly. The behavior of the liquid oxygen may be contrasted with that of liquids like water, which extinguish fire; and that of liquids like gasoline, which burn.

Experiment 17.—Take a piece of charcoal held in a pair of tongs, and touch it to a flame until it is kindled, and then insert it into some liquid oxygen. The charcoal burns beneath the surface of the oxygen with an intense light, due to the production of a temperature of approximately 2000°C. The contrast of this high temperature with that of the surrounding liquid oxygen (−183°C.), separated by only a small fraction of an inch, is startling.

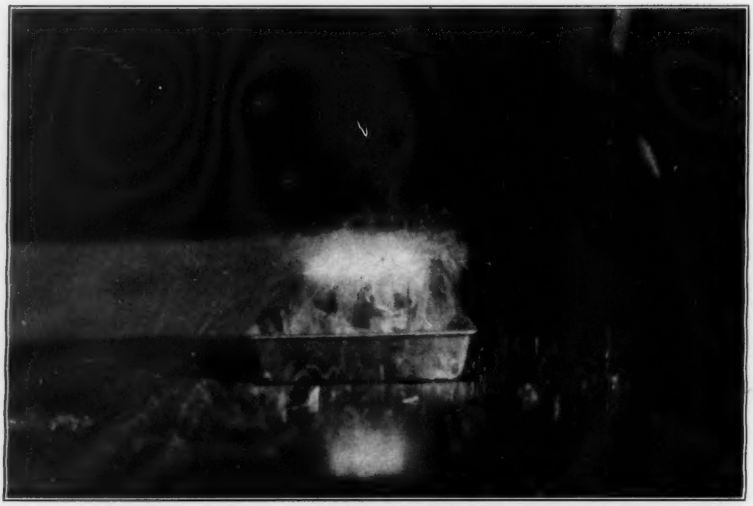
Experiment 18.—Remove the cigar from the liquid oxygen, and bring the end in contact with the flame. The cigar takes fire and burns with a long flame like a firework. The combustion is so rapid and so complete that even the odor is consumed. The author always holds the cigar



WATCH SPRING BURNING IN LIQUID OXYGEN

in a pair of tongs, because, while he has seen hundreds burn quietly, he is always expecting that sooner or later one will explode.

Experiment 19.—The old familiar experiment of burning steel may be carried out, using liquid oxygen. We find that a watch spring is much superior to a piece of picture wire for this experiment, because the spring throws off brilliant sparks. A number of springs should be prepared by stretching them out straight, and running them through a flame to remove the temper. Then break off the end of the spring where it fastens to the watch, wrap two turns of cotton string around the spring near each end, and tie. Dip the ends of the spring in melted sulfur, and allow to cool. By putting the sulfur at each end, one gets two chances to kindle each spring. For this experiment, we use an iron sand-bath, about 12 cm. in diameter. This dish is placed on the block of ice used in experiment 13, and the side of the bath farthest from the audience is elevated somewhat by putting something under it. Some liquid oxygen is then poured into the sand-bath. The sulfur on the end of the watch spring is lighted, and this end introduced into the liquid oxygen. If the latter is practically free from nitrogen, the spring burns rapidly, and should be fed down into the liquid oxygen as it burns away, taking care not to touch the dish with the burning spring. If, for any reason, the first spring fails to burn satisfactorily, try another, because soon the oxygen will purify itself, and the spring burn spectacularly. It is advisable to wear glasses or goggles during this experiment, because the author has occasionally found bits of iron oxide fused into the lens of his glasses after a demonstration.



SPARKS FROM IRON DISH AFTER BURNING ALUMINUM IN LIQUID OXYGEN

Experiment 20.—Perhaps the most spectacular of all the experiments is the burning of powdered aluminum. We perform it as follows. First make sure that there is no fire or sparks anywhere near the experiment. Then place the iron sand-bath used in experiment 19 in a level position on the block of ice, and put into the dish 30 to 50 cc. of powdered aluminum (bronzing powder). Wet this down with liquid oxygen, using enough so that the aluminum is covered with liquid oxygen. Place a small candle in a candle holder two feet or more in length; light the candle; and keep close watch of the contents of the dish. As soon as the last drop of liquid oxygen disappears, and the still moist aluminum begins to form craters and to resemble a pancake ready to be turned, apply the candle flame to the aluminum near the center of the dish. Have your eyes narrowed to a slit, and the instant you see that the aluminum has taken fire, close them completely and step back.

If you have caught the right moment for setting off the aluminum, it will burn with a blinding flash; and if you have been liberal with the aluminum powder, the dish will be largely burned and melted, and the molten oxide and metal will fall as a shower onto the table and the floor. The temperature change during the very brief period of burnings is exceedingly great, because it goes from $-183°C.$, the boiling point of liquid oxygen, to a temperature above the melting point of tungsten, $3400°C.$ The high temperature reached is the cause of the blinding light. This

light is so strong that it seems wise to caution the audience that those having very sensitive eyes should partially close them or look away.

Experiment 21.—Other combustible substances, such as powdered charcoal, cotton, etc., when mixed with the proper amount of liquid oxygen, will burn with explosive rapidity in the open, and will actually explode violently if confined, or set off with a fulminating cap. The ratio of combustible to oxygen must be adjusted within narrow limits, as either too much or too little oxygen would give disappointing results. These points may be illustrated by taking about four grams of cotton, soaking it in liquid oxygen, allowing it to drain, and then placing it in a sand-bath. Pinch the cotton lightly between the fingers from time to time, and when it feels as though about all the liquid oxygen had evaporated, set fire to the cotton with a candle in a candle holder. If the proper quantity of oxygen is present, the flame will run rather slowly over the outside of the cotton where there is too little oxygen, and then a puff of fire will consume the bulk of the cotton, where the ratio of the cotton to the oxygen is just right; and a small amount of cotton will be scattered about in tufts, unburned because of too much liquid oxygen. That oxygen is still present in these tufts may be demonstrated from their rapid combustion upon the application of the candle flame. The part that burns with a puff would explode violently under the influence of a fulminating cap. This experiment should be performed only in fireproof surroundings because smoldering cotton is scattered around.

A mixture of liquid oxygen and liquid methane explodes with extreme violence, and the same is true of other hydrocarbons and liquid oxygen; so care must be taken not to use oxygen for combustion experiments which has been used with alcohol or kerosene experiments. The intensity of the reaction between liquid oxygen and hydrocarbons makes credible the recent news item that an engine weighing only fourteen pounds had developed 200 horsepower when operating on a mixture of gasoline and liquid air.

Experiment 22.—Liquid oxygen is distinctly magnetic. This may be shown by suspending a small flask by a string about a meter long, so that the flask is free to swing, and then placing near the flask a powerful electromagnet with a switch in the electric circuit.

Fill the flask with liquid oxygen; close the circuit. The flask will be slightly attracted toward the magnet, and will move barely perceptibly. As soon as it has reached the end of its movement, open the switch, and let it swing back. When it starts toward the magnet once more, close the switch, and the flask will swing farther than it did the first time. Repetition of this process will finally build up a swing that all can see. Have ready a carpet tack, and when the audience has been convinced that oxygen is attracted toward the magnet, drop a single tack into the flask

and turn on the magnet. If the latter is of the proper strength, the flask and its contents will be drawn immediately to the face of the magnet and stay there.

A five-cent coin is just enough more magnetically permeable than the air so that if it is freely suspended by a silk fiber it will set itself parallel to the magnetic lines of force between the poles of a powerful electromagnet. Surround it, while in this field, by liquid oxygen, and the coil will turn and place itself across the lines of force, showing that liquid oxygen has a greater magnetic permeability than the coin. For success in this experiment, the magnet must be very strong, and the oxygen must be kept from boiling by surrounding it with liquid air. Of course, the coin must be fastened to a wire that will project above the liquid oxygen, and this wire must be provided with a straw or other light pointer to indicate the position of the coin.

Applications of Liquid Air

The largest single use for liquid air is in the commercial production of oxygen which, as stated above, involves the liquefaction of the air and its fractional distillation. At the same time that the oxygen is secured the more volatile constituents of the air (helium, neon, and nitrogen) may be concentrated in one portion and the less volatile (argon, krypton, and xenon) in another. Therefore, these gases, with the exception of helium, are chiefly by-products of the oxygen industry.

Neon for neon signs is concentrated by the fractional distillation of the more volatile portions of the air and purified by removing the nitrogen with hot magnesium or calcium. Any argon, krypton, or xenon present is then adsorbed by cocoanut charcoal cooled to $-100°$C., and the neon adsorbed in large amounts of charcoal cooled with liquid air. The unadsorbed helium is pumped off and the charcoal warmed to recover the neon.

Argon is used in surprisingly large quantities for making the gas-filled incandescent lamp bulbs. It is present up to about 3% in commercial oxygen and may be concentrated by careful distillation of the oxygen fraction of the air, followed by purification with the hot copper to remove the oxygen and hot magnesium or calcium to eliminate the nitrogen. Other inert gases may be separated from the argon by fractional distillation or selective adsorption in cooled charcoal. Krypton and xenon accumulate in the least volatile portion of the liquid air and may be obtained from this source. Of course, the main product of the fractional distillation of air besides oxygen is nitrogen of commercial purity.

The explosive property of mixtures of liquid oxygen and combustibles has been successfully applied for industrial blasting. One of the developers of this process states that they have installed in Chile six vacuum-jacketed

storage tanks for liquid oxygen, each holding 1000 gallons, this oxygen to be used in explosives.

Liquid oxygen is sometimes carried by aviators to supply the oxygen needed by man and occasionally by engines at very high altitudes.

One very important application for liquid air is its use as an aid in research. It is a very useful agent for this purpose, largely because of its low temperature. If temperatures no lower than −78.5°C. are needed they may be secured more economically by dry ice than by liquid air. We may safely predict that liquid air will never be used extensively for ordinary refrigeration nor for the transmission of power, because it is too expensive and too inefficient.

Cemented Shoes. For over fifteen years, shoes have been made in Europe with cement taking the place of stitching for the attachment of the sole. Every little while, a flurry is created in this country when it is announced that a cemented shoe is about to be made here. Not a few imagine that this type of shoe will revolutionize some branches of shoe manufacture and perhaps greatly cheapen shoes.

It now appears that the shoe with cemented-on sole has actually found its place in America. It does not promise to attain the proportions of a revolution. It is entering the field here as an interesting variation in the art, rather than as part of a radical and new system of shoe-building. The cementing-on process appears to be best suited for McKay shoes, but is also applicable, with modifications, to turn shoes and even to welt shoes. Its present and most natural field is for women's "high-style" shoes.

With the cemented shoe it is not necessary to remove and re-insert the last during the shoe-building process, as it is with McKay and turn shoes. Consequently, the folds and wrinkles so hard to avoid when the last is disturbed, are avoided, and lining, insole, upper, and outsole are virtually molded into shape. Such excellent shaping makes this type of construction desirable for ladies' light-weight and novelty shoes.

A distinct advantage of the cemented-on sole, besides the excellent shaping and fit which are more or less characteristic of the method, is that no staining or injuring of the leather or lining can take place since the shoe is built dry throughout. A disadvantage of the cementing process is that it calls for the use of more upper leather than does stitching, to give sufficient surface for adhesion to the sole. Sole leather can be suitably flexed and otherwise handled and treated to give a pliable, comfortable shoe.

The parts of the leather to be cemented must be specially buffed to produce a surface of maximum grip, and care is needed throughout the manufacturing process to insure good adhesion. With good workmanship, a satisfactorily strong shoe is produced.

Some features of cemented construction are cheaper than corresponding features of stitched construction and some are more expensive, taking all things into account. The complete cost of the cemented-sole shoe need not be greatly different from that of the stitched shoe, although the present practice appears to be to make the fancier grades at relatively higher cost levels.

Whether or not the shoe with cemented-on sole will find more than a temporary or a nominal place in the art will depend perhaps most of all on customer acceptance. The shoes are stylish and comfortable, but it remains to be seen whether or not cemented construction, when known to be such, will be considered as the psychological equivalent of stitching.—*Ind. Bull. of Arthur D. Little, Inc.*

BERNARD PALISSY
From a painting on vellum, Cluny Musée, 1592.

BERNARD PALISSY, SIXTEENTH-CENTURY SCIENTIST

MARY LOUISE FOSTER, SMITH COLLEGE, NORTHAMPTON, MASSACHUSETTS

Bernard Palissy was born in 1510 in the southwestern part of France, a region whose equable climate and fertile fields had always attracted invaders. Consequent unrest had bred in its inhabitants at the end of the sixteenth century an independent spirit and imagination to an unusual degree. With slight formal education, but skilled in the craft of glass-making, Palissy spent some fifteen years traveling and studying natural phenomena before he settled in Saintes. Then, inspired by the sight of a beautiful vase of Italian faïence, he began his work as a potter. After a painful struggle of fifteen years, he was successful in making a beautiful glazed earthenware. In 1575 he gave lectures on his theories of earth formation, solvent power of water, crystallization, and agriculture to the most distinguished men of Paris. He was hanged as a heretic in 1589.

. . . . . .

France, at the beginning of the sixteenth century, felt youth and springtime in her heart. Louis XII, so beloved that he was called the "Father of his People," was king. His policy of peace at home had brought happiness and comparative plenty, in spite of many foreign wars that were both ill-advised and costly, and his reign was to see the final triumph of national independence and national unity. Feudalism was at an end.

Leisure and prosperity and the printed book were the powerful forces that underlay the Renaissance. In an edict of 1513, Louis said of printing that its invention "seemed more divine than human." Besides this tremendous stimulation of the imagination caused by the circulating books, the spread of Greek philosophy through the Arabic civilization and the discoveries of Columbus created a new point of view, an awakened curiosity demanding for its satisfaction, not fictitious tales, but facts, accounts of actual experiences, stories of natural phenomena. It was the dawn of the Scientific Age.

While all parts of France were feeling the influences of the new culture, most of all did the southwestern region thrill to these stirring currents of thought. The favorable physical conditions, temperate climate, low mountains, abundant streams, and fertile valleys had attracted from most remote times invading tribes and nations. Here the Romans had one of their most important proconsular provinces. Following the Romans came the tribes from the North; then the French and English fought for territory; and finally came the struggles of the Reformation. Destructive to normal peaceful living as was this constant warfare, it did breed an independent spirit in its people, revealed in the demand for civic liberties and in the genius which flowered in its poets and writers.

It was in this region and at this time, both so auspicious for the nurture of genius, that Bernard Palissy was born. The precise date of his birth

is not known; it was about 1510. The place, too, is disputed, but is supposed to be Agen in Agenais. Of his family he says he was a "lowly person of humble state." However that may be, during his life he "knew all the extremes of human existence: son of an artisan, he became the protegé of kings."

His formal education was most meager, according to his own account. He frequently regrets that he knew "neither Greek nor rhetoric, but was a simple artisan poorly instructed in letters." However, he was an intelligent boy and what he lacked in formal education he made up for with keen powers of observation and an insatiable curiosity concerning natural phenomena, their causes and relations. Alchemy he learned "with his teeth." In geometry he assures us he was "not deficient," and of surveying he tells us "they thought I was more learned in the art of drawing than I was, a fact which often caused me to be called to make a survey of land in dispute." There is a legend of a land surveyor who was fond of him as a child and who took him as apprentice and assistant in carrying the rod. He himself says: "I have had no other book but the Heavens and the Earth which are known to all and to all it is given to study and read this beautiful book. So, having read it, I have considered terrestrial matters; because I have never studied astrology and the stars, that has been the book I have pored over."

From his childhood Palissy worked at glass-making. There is support for the belief that he learned the art of coloring glass from his father. He was familiar with all the processes: the grinding of the colors and the mixing of them for staining and finally the application of them upon the glass. "Experience, which is mistress of the Arts," he says, "has long since made me acquainted with the fact that iron, silver, lead, and antimony can make only yellow." The reference to antimony shows clearly his intimate knowledge of certain chemical reactions familiar only to the alchemists of the day. "I have seen the time," he says, "when the glass-workers were in great demand because they made the faces for the windows in the churches. Those who painted said faces did not dare eat garlic nor onions, for, if they had done so, the paint would not have adhered to the glass. . . . The profession of glass-making is honorable and the men who pursue it of good repute."

Our eager young artisan worked hard at his trade for some years. Furthermore, he knew all the native flowers, the agricultural methods used by the farmers of Agenais, the near-by mines where he found minerals for his palette, and the fish in the streams. His interest in all natural phenomena drew him inevitably toward that unknown world that lay beyond the horizon.

When his journeys began, we do not know. He was about thirty when they ended. During that time he visited most of France south of Paris

and trained himself in true scientific method by observation and experience. He went with "bent head in order to scrutinize the works of Nature," wherein he found the "beautiful secrets" he was so keen to know. Everything was of interest to young Bernard. With "great effort, not in a few days by reading books, but by anatomizing the matrix of the earth" he informed himself about those natural phenomena, the springs, the caves and caverns, all so numerous in this region. Underground, in the caves he found abundant streams and springs. Farther on he met these same streams gushing forth above ground. And so, at the very outset of his youthful wanderings, he began to study the influence of water in the formation of the earth, its nutritive value for plants and animals, and its causative relation to other natural phenomena. He himself tells that he went farther than mere observation as he "walked with bent head, the whole way, in order to see nothing which might prevent me from imagining what could be the cause," seeking indeed a reasonable explanation for these familiar appearances. "These years of travel were for him," says Duplessy, "a sort of emancipation. In the continual change of region he threw off the scholastic yoke, involuntarily, without doubt, but in any case to his own advantage; had he settled down in some city, he would soon have paid the tribute of his presence to some branch of alchemy or of scholasticism. Who knows if he would ever have escaped?"

In the valley of the Lot and Tarn he must have lingered a long time. He speaks of it often and lovingly as a "city of refuge in the evil days of peril." Here were the flourishing towns of Albi and Moissac. In the former is the beautiful cathedral of Sainte Cecile with its rood screen sculptured like lace and its richly adorned ambulatory. At the time when Palissy visited it, the statues of angels and prophets and Old Testament characters had just been finished by order of Bishop Louis d'Amboise and his nephew.

Here in this pleasant land Palissy created his "Delightful Garden." The little book describing it was written many years later when his exhausting struggles in faïence-making and his participation in the religious wars had brought weariness to mind and body. Memory recalled the peaceful valleys and the beautiful hills. With such pleasant thoughts the ideal garden with fountains and grottoes was designed. But memory also recalled the desolateness and misery of the farming community and its need of education in agriculture. In his opinion,

> There is no art in the world for which one needs more understanding than for agriculture and I assure you that if farming is carried on without understanding, it is a daily violation of the earth. Truly, I wonder that the earth and its natural products do not cry vengeance on certain murderers, ignorant and ungrateful men, who, without reason, daily waste and destroy trees and plants. I dare also to declare to you that if the earth is properly cultivated, carefully tilled as it should be, one acre will produce more than

two acres can with the present methods..... The ignorant practices which we see committed every day in the name of agriculture have many times tormented my spirit and angered me because I see how a man aggrandizes himself by sucking substance from the earth without giving it in return sustenance. It distresses me to see the great, who should be intelligent, leave their farms in the hands of ignoramuses. Thus it follows that the earth and what it produces is often poor and great harm is done the animals whom God has created for man's comfort.

He calls himself "an amateur of agriculture" but he was much more like our modern farmer, trained in scientific methods of fertilization of the soil and keen for maximum production.

In Auch, an important episcopal town, capital of Gascony, our young apprentice undoubtedly had a chance to work on the magnificent stained-glass windows which were made by Armand Desmoles. We may read thereon the date "25 June, 1525." These windows, twenty in number and measuring forty-five by fifteen feet, depict the Prophets clad in gorgeous robes of red, blue, or purple, with temples and hills in the background. Palissy often speaks of the "marvellously beautiful blue" obtained from the "saphre" used by glass-workers, "a color given by no other stone." He defines the mineral as an "earth which is found in gold mines and which is an earth fixed like gold and from which the blue color in enamel is made."

This he further elaborates, saying:

I know no plant nor mineral nor any stuff which can color stones blue except saphre, which is a mineral substance extracted from gold, silver, and copper. In the natural state it shows very little other color than grey shading slightly on the violet. However, when it is fused with glass, it makes a wonderfully beautiful blue. Hence one may say that all stones having a blue color have got that color from saphre.

This mineral was undoubtedly some compound of cobalt, often found associated with gold and silver. Other colors, yellow and red, he describes in detail. All of these were used by Desmoles with brilliant effect.

From Gascony Bernard went to the Pyrenees, where he spent several years, pondering over the phenomena of hot springs and salt springs. Of the medicinal value of these springs he was most skeptical, attributing the enlarged throats of the inhabitants to the dissolved salts which were too likely to vary from year to year for the spring to have any specific curative value.

In regard to his theory about hot springs, he says:

The Book of the Philosophers, in which I have learned all these wonderful secrets is nothing more than a kettle half-full of water, which, as it boils and so is a little roughly stirred by the heat at the bottom of the kettle, rises even to the top of the pot. It can only be that there was some vapor generated within the water by virtue of the heat, inasmuch as the kettle was only half-full when it was cold but was full when it was hot. The furnaces in which I bake my batches (of pottery) have given me many opportunities to become acquainted with the energy of heat. Among other experiments which have interpreted to me the elemental forces which might cause earthquakes, I have con-

sidered a ball of brass, which, when heated over charcoal with a little water, will suddenly send out a vapor which will cause the wood to burst into flame, even though this has been freshly cut.

Cap notes that Palissy reveals in this statement acquaintance with Vitruvius, the great Roman architect who was being very much quoted at that time. In the seventeenth century, Boyle used the same experiment in connection with the combustion of wood.

Many queer notions about natural phenomena were prevalent during the Middle Ages and among them were some concerning the origin of springs and rivers which seemed often to gush forth from the solid rock. It was believed that they were engendered in the mountain caverns from the air, which had dissolved into water. Years later Maître Bernard insists:

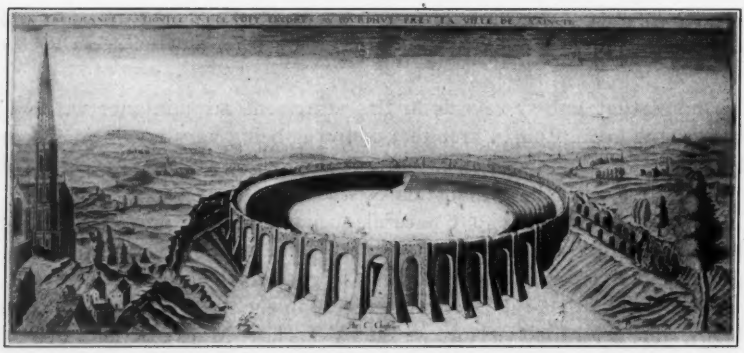
Instead, I know for a fact that the enormous amount of water that pours out from the hollows in the rocks and mountains and is seen to issue like a great smoke that rises and makes the atmosphere heavy, spreading itself in all directions, is nothing else but rain when said vapor condenses. I have often seen such heavy vapors arise in the Ardennes country, and those who saw them come out as I did, said in a little while we should have rain, for they were convinced that the vapors condensed themselves into rain. In the Pyrenees I have many times seen such vapors go forth and rise on high where they were frozen into snow which soon fell and covered the ground.

I do not, however, deny that the aqueous vapors of the subterranean caverns may contain great quantities of water, but it must necessarily be that they have been put there by the couriers and messengers of God, *i. e.*, the winds, rains, storms, and tempests, for it is written that these are the heralds of the justice of God. In very truth, the waters of the caverns have been put there by the rains derived from the water which rises from the sea, from the earth, and from all moist things which in drying produce the aqueous vapors that are raised on high to fall again. Thus the waters never cease to rise and fall. As the sun and moon do not rest, similarly, the waters never cease to work, creating, going to-and-fro, as God has commanded.

Additional proof that spring water did not come directly from the sea, he found in its freshness, and its location on mountain sides high above sea level. He insisted that the rain-water percolated through the earth, finally finding its way to the surface again through the crevices and interstices in the strata of the earth. He was the first to attribute spring formation to the filtration of rain-water through the earth.

Maître Bernard continues,

It is necessary, then, that you assume as a certainty that all the waters which are in the world and ever shall be, were created in the same day. And if this is true of the waters, then, too, the constituents of the metals and of all the minerals and stones were also created on the same day and whatsoever else there is of earth, air, and heat, for the Sovereign Creator has left no void and, as He is perfect, so He has left nothing imperfect. But He has bidden Nature to work, to produce, to create, and to consume, and to recreate. Though you see that the fire consumes many things, nevertheless it also nourishes and sustains many things. The everflowing waters spread and scatter many things. Without them, I contend, nothing could ever exist. And so, though the fire and water destroy on the one hand, on the other they create and produce.



SAINTES FROM AN OLD PRINT

We find here, clearly stated at the end of the sixteenth century, the theory of the conservation of matter. The thought is expressed in biblical language. It is probable that Palissy during his journeys to and fro had been won over by the itinerant preachers to the reform religion.

Palissy continued his travels and explorations into natural and physical phenomena until about 1539, when we find him settled in Saintes on the Charente. At that time, Saintes was the capital of Saintonge, the seat of a rich bishopric, and an important industrial center. The salt marshes in the neighborhood were a source of generous income to both the king and the inhabitants. But it was a hotbed of strife and rebellion due to heavy taxation and religious discontent. The peaceful meadows, where, says Palissy, "I was wont to walk the length of the beeches, and, as I paced beneath their shade, heard the gentle murmur of the waters of the stream which flowed at their foot, and from the other side the voices of the birds which were in the trees," became later the scene of much bloodshed.

Nearby, Bernard Palissy located his home. Glass-making, no longer a lucrative craft, and surveying furnished but meager living to his growing family. Much time was spent in studying the animal life of the region, both land and aquatic, while religious discussion and active participation in the spread of the reform doctrines furnished further occupation. In connection with this movement he became acquainted with the Pons family, co-religionists, recently returned from Ferrara from whose court they had been banished for their adherence to Calvin and Protestantism.

Sire de Pons was a man of consequence in Saintonge and numbered among his friends and relatives men and women of influence in royal circles. Among these Palissy made many friends who became later, in a season of great need, powerful and resourceful supporters. Here, too,

in the beautiful château de Pons, richly adorned with many objects of Italian art, Palissy found "*une coupe de terre tournée et esmaillée d'une telle beauté*" that he became possessed with an overwhelming desire to create a similar one. He saw opportunity to manufacture a peasant pottery to replace the metal ware in use. His skill in glass-making led him to think that the task would not be difficult and his straitened financial condition encouraged him to make the venture. So, near the murmuring beeches, he set up his kiln.

In his book published many years later, Palissy tells of his first experience as an industrial chemist.

> Without knowing in what way these enamels were made, in those days I powdered every sort of matter which I thought might make a glaze. When I had ground this up, I bought a quantity of earthen jars which I broke in pieces and upon them put the stuff that I had ground up. Then, having marked them and made a memorandum of the composition with which I had coated each fragment and having made a furnace to my liking, I put these pieces in to bake, in order to see if my formula would in any instance make a white glaze, for I was looking only for a white enamel because I had heard it said white was the foundation of all glazes.
>
> Now, because I had never seen clay baked and did not know at what degree of heat the clay would melt, it was impossible for me to do anything that way and be sure that my mixtures had been good, because sometimes the batch was overheated and sometimes underheated. And when the aforesaid objects were too little baked or dried, I could not at all tell what was the precise reason for failure. I put the blame on the material, whereas, if I could have made the temperature such as the materials required, the experiment might sometimes have been successful; or, at least, I might have found some indication by which to modify the procedure.

Years of experiment during which successes were interspersed with heart-breaking failures, just often enough to prevent him from complete relinquishment of his project, lay before Palissy. By bitter experience he learned the difference in coarse and fine clays, and especially the importance of their water content. Many mishaps taught him the necessity of raising the temperature gradually, so that the moisture went out by degrees:

> . . . for, if the workmen do not expel the volatile vapor, which is in the clay, little by little, but instead make a great heat before it has been driven out, there is nothing more certain than that the heat and the moisture on meeting will cause an explosion in consequence of their opposite nature. Indeed, I am convinced that natural explosions are brought to pass in the same way: to wit, by heat and moisture, because they are antagonistic and cannot exist together. The fire, since it is strongest, finding the moisture enclosed in the particles of earth, wishes to drive it out violently as one would an enemy, and the moisture being hardpressed, wishes to escape with all diligence; but inasmuch as the heat does not give it time to find the little doors by which it entered, it is forced to flee and in fleeing it causes the stones in which it was enclosed to split and break.
>
> For such slow removal of the moisture, days and nights of heating at a low temperature are necessary, and woe betide the weary watcher who falls asleep and lets the fire

get low or go out. No amount of tardy attention will save the batch! No, not even if the desperate workman pile in all the wood of the Ardennes forests. The damage is done and there is nothing for it but to begin over again. Great has been the loss on this account. It is impossible to make pottery in a hurry, for the destruction through impatience may be very great. Furthermore, the coarseness or fineness of the clay makes a difference in the time and degree of heating. I once found a clay in Poitou and worked on it for well over six months before I had my batch complete because the vessels which I was making were very elaborate and expensive. Now, while I was making these dishes of the aforementioned Poitou clay, I made some also of Saintonge clay which I had used several years before. I was, therefore, acquainted with the degree of heat proper for that clay and, thinking that all clays could be baked at the same temperature, I had my batch of Poitou clay baked along with that of the Saintonge clay, thereby causing myself great loss; for, when the batch of Saintonge clay was sufficiently baked, I thought the other would be, too. However, when I came to glaze my dishes, some of the vessels began to dissolve and crumble to bits as would a lump of chalk soaked in water, whereas the dishes of the Saintonge clay, baked in the same oven with the same degree of heat and for the same time behaved very well. And that is why a man who works in clay is apprehensive of the unknown nature and diversity of clay.

After many failures with his own kiln, he resolved to send his trial pieces, some three or four hundred in number, to a neighboring kiln. He had no better luck than before. The temperature was too low and the pieces had been put into the oven without due attention to the arrangement. It was impossible to draw any conclusions. Was it the temperature that was wrong? Or the composition of the glaze? Or the proportions of the mixture? Nothing but shame and sadness, and loss of time and money resulted from the experiment. Palissy's discouragement was so complete that he resolved to quit his search for the wonderful enamel and devote himself solely to making a living.

It was just at this time in May, 1543, that Francis I published an edict at St. Germain-en-Laye ordering that the salt tax be levied and collected at the salt marshes. This necessitated a survey of these lands, which were very extensive in Saintonge. Palissy's well-known skill in this line led to his appointment as surveyor of the whole district. The work was well paid and lasted a year or more. He was directly under the supervision of Guy de Chabot, Baron de Jarnac, Governor of Rochelle and mayor of Bordeaux. This was an association which brought Palissy much pleasure and later, when he was in danger of his life, much needed assistance. Palissy's gentle spirit, idealism, and simple nature always won him friends among the cultured classes; while the same qualities made the ignorant call him a fool, lacking in common sense.

Palissy has left us a vivid description of the salt marshes of Saintonge as he knew them. The transformation of the marsh land into a productive plant of immense proportions, the process of salt-making by evaporation, and the method of transportation of the finished article are set forth with precision. With characteristic thoroughness, the while

he did his task of surveying, he studied the associated phenomena: the nature of common salt, of the tides, of the strata of the earth in the region, and of the tiny marine life. And from these he began to formulate a theory of salts in the more general sense and of their relation to the animal and vegetable kingdoms. The summer of 1543 proved to be dry and he worked hard on the survey of these intricate marshlands; and, during the following winter, when the marshes were flooded, he mapped the neighboring towns and villages. "Then, when the task was done," he naïvely tells us, "and I found myself supplied with a little money, I yielded again to my longing to make a white enamel!"

Among the many possible causes for his failure to effect a fusion of the mixtures with which he had coated the trial pieces, Palissy had come to the conclusion that the factor of temperature was the most important. The furnaces which he had built had failed. Likewise those of the potters. There was still the furnace of the glass-workers whose ovens made use of a much greater heat.

Accordingly he determined to repeat his former method of preparation but to change radically the temperature. He broke into bits a dozen clay pots, brushed each with a carefully prepared mixture, labeled each piece, recording the composition of the wash with which it was covered, and set out for the glass-makers' furnace. There were some two or three hundred pieces, only one or two, however, being covered with the same mixture. The next day when he drew out his batch, he had his reward. Some of the mixtures had begun to melt! One shard even bore a trace of the precious, the long-sought white enamel.

Here was just cause for rejoicing and encouragement. Victory seemed sure at last, and with fresh energy, begot of enthusiasm, he continued to work. Back and forth from his little shack in the Faubourg des Roches to the glass-workers' furnace he went day after day. With some of the precious earnings he hired a man to fetch and carry the trial bits. For more than two years he worked without again getting the necessary combination of temperature and constituents in the right proportions!

Finally he could bear it no longer. For the last time they put their trial batch into the oven. Funds were exhausted. Two children had died and the rest were sick and hungry. He himself was worn out. "Then, by the grace of God, just as I had lost courage," he writes, "I found one of the trial pieces which had melted within four hours after it was put into the oven, one single piece covered with a glaze that was white and highly polished, a white enamel, singularly beautiful, so that I was filled with such joy that I became a new man." Nothing seemed impossible and Palissy set to work with renewed vigor.

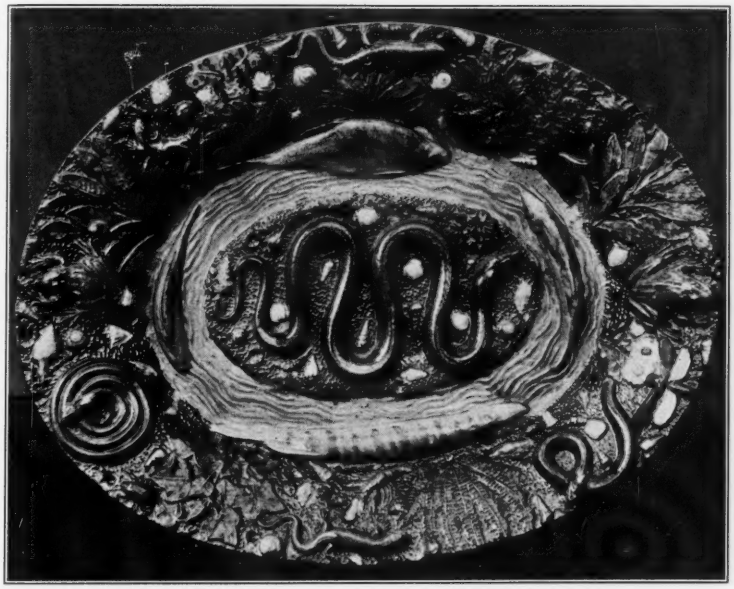
Again it was the details which delayed the accomplishment of his plans. With indescribable labor he built a furnace as like that of the glass-workers

as possible, doing all the masonry himself, mixing the mortar, drawing the water, and carrying the bricks on his back. There was no money to employ even a single man to help in this heavy work. Finally the furnace was finished and the new jars put into the oven. They went through the first baking successfully.

The glaze was the next operation. Night and day Palissy worked, powdering material like that from which he had obtained the beautiful white enamel in the glass-worker's furnace. This he spread upon the jars, which he then put into the oven. He lighted the fire hopefully. Alas, his apprenticeship in this new craft was not yet over! Hard as had been his experience hitherto, the greatest disaster of all was still to come. In a heart-rending story he gives an account of this latest experiment.

> Then I put my jars into the oven to melt the mixture with which I had covered them. That was a most unhappy experience for me. Although I tended the furnace for six days and six nights without ever ceasing to shove wood into the two openings, it was impossible to make that wash melt. I was like a mad man. I was worn out with the labor, but I realized only too well that in my mixture there was too little of the substance which had made the others melt. And so I began at once to grind and powder some of that substance, without once letting my furnace cool down. Thus I had a double task: to grind and powder the extra material, and to keep up the fire in the furnace.
>
> When I had thus compounded the new mixture, I was forced to hurry off and buy some jars on which to make trial, for I had lost all the jars which I had made myself. And having covered the new jars with the preparation, I put them into the oven, all the time holding the fire at its greatest heat. And then occurred another mishap of the most distressing nature: my wood gave out! There was nothing to do but burn the supports which held up the young trees in the garden; soon these were consumed: then the tables were fed in; and finally I had to rip up the flooring of my house in order to make that second mixture melt.
>
> It is impossible to describe to you my state of mind. I was quite exhausted and emaciated. The work had been heavy and the fire hot. For more than a month my shirt had not been dry on me! Then, too, by way of consolation, they laughed at me and those who should have aided me did actually go through the city crying out that I was burning up the floor. And so I lost my credit and was rated a fool. Still others said I was trying to make counterfeit money, a libel that made me sick. I went through the streets like a man ashamed. I had run in debt in several places: usually there were two children with the nurses whose wages I was unable to pay. And still no one was aiding me. On the contrary they mocked me, saying, "he would better die since he has quit working at his trade."

However, driven on by the longing to make that "beautiful white enamel," contrary to the advice of common sense, and in spite of utter weariness of mind and body, Palissy determined to try again. Once more the furnace was re-built, the jars coated with the mixture for glazing, the fire started, and the jars put into the oven. This time there was a most unforeseen disaster. The mortar used to build the furnace had contained pebbles which, at the very moment when the glaze was liquefied by



FAÏENCE OF BERNARD PALISSY
No. 2485, Musée de Cluny, XVIes.

the heat, were driven explosively out of the mortar and perversely alighted on the moist glaze. Every piece was marred by adhering splinters of stone.

But perseverance conquered and one after another all the difficulties were overcome: muffs were made to protect the jars from flying ash; the temperature was regulated by means of little clay figures, a method still used by the potters of Limoges. Experience had taught him. He learned from his failures, costly but efficacious. It had taken fifteen or sixteen years to overcome all the difficulties.

The composition of these wonderful glazes Palissy refused to reveal. A truly modern industrial chemist, he appreciated to the full the economic value of his discoveries. He says,

> The mistakes I have made in the quantities used in my glazes have worked to my advantage. Therefore, I am of the opinion that every man should strive to find the dosage for himself, as I have done, otherwise the knowledge will be too cheap, a reason some hold for despising learning. I am of the opinion that there are no people in the world who cheapen research and craftsmanship except those whom it has cost little, whereas those who have practiced it at great expense and labor do not treat it so lightly.

His studio-workshop became a very busy place, executing orders, making new designs, and extending the market for the lovely faïence. His two

sons, Marthurin and Nicolas, assisted him. The type of pottery which this kiln produced is known to us from the collections in the Louvre, the Cluny Museum, and the Sévres Museum. The colors of the plates, platters, jars, and pitchers vary from a brilliant green to blue and grey. The decorations and designs on the dishes made while he was still living in Saintes are based on his studies in natural history: on fish, lizards, snakes, shells, leaves, and ferns, all the living things which he was accustomed to see on his walks through the meadows and along the shore. At a later period, the forms were those near Paris. "One would say," says Lamartine, "that a housewife, in washing her dishes had dipped one of these plates into the sea and withdrawn it filled to the brim with sand, shells, débris of grass and aquatic animals."

At the same time that Palissy was struggling to make his glazed earthenware, he was also taking an active part in the struggles of "the little church at Saintes," a reform church founded about 1546. Calvin as well as many other itinerant preachers from Geneva had received sympathetic reception in all parts of Saintonge. Persecution of the reformers, reprisals, and even death by fire were of frequent occurrence.

Furthermore, the increased salt taxes imposed by Henri II in 1547 had stirred up discontent with resultant riots in adjoining provinces. Finally, Anne de Montmorency was sent with a strong force to suppress the rebellion. This was done and the people of Saintes were allowed to purchase freedom from the salt tax by payment of 200,000 gold dollars, plus the cost of the war.

Anne de Montmorency did more than suppress the rebellion. He discovered Palissy working in his old tumbledown shack, trying to build kilns and make glazed tiles and pottery. He built a studio-workshop for our potter and ordered tiles for his new palace at Ecouen, for which Palissy received an annual stipend of 1200 livres. Still another powerful patron was Louis de Bourbon, Duke de Montpensier, who secured the workshop from the intrusion of fanatic religious enemies.

Religious troubles continued to increase. In the bitter feeling engendered by persecution and reprisals, finally even the powerful protection of the Duke de Montpensier was unable to save Palissy from arrest and he was hurried by obscure roads to Bordeaux. An attack was made on the studio and a plan was already in progress for its complete destruction when more powerful friends came to his rescue. Through the agency of Montmorency, the Queen Mother, Catherine de Médicis, was persuaded to appoint "Bernard Palissy, Inventor of Rustic Earthenware to the King and to the Duke de Montmorency, Constable of France." This appointment at once took him out of the jurisdiction of the antagonistic courts of Bordeaux. It added immeasurably to the prestige of the poor artisan, who called himself a "Worker in Clay." He began to be

Faïence of Bernard Palissy No. 3107, Musée de Cluny

called "Maître Bernard" and esteemed as an artist of great originality.

In 1563, Maître Bernard, while still in Saintes, published a little pamphlet of some hundred pages, entitled "Recepte véritable." Only two copies are known to be in existence: one in the Bibliothèque royale and the other in the Bibliothèque de l'Arsenal in Paris. They are treasured among the archives as the unique record of a highly intelligent, original thinker of the sixteenth century. The book is a talk on science, an informal conversation between "Demande," the unobservant, conservative person, and "Réponse," who presents Palissy's theories and experiments.

In 1564, the Court left Fontainebleau for a tour of the provinces, arriving in November at Saintonge. It was at this time that Catherine de Médicis probably saw Maître Bernard's beautiful tiles and faïence and seized the opportunity of securing this original artisan to work on the new palace of the Tuileries, which she was even then planning.

Two years later Palissy left Saintes forever and took up his residence in Paris in the rue du Dragon. A statue of Palissy has been erected by the city of Paris in the Square near Saint-Germain-des-Prés, the former location of the rue du Dragon. He was known as "Maître Bernard Palissy, governor of the Tuileries," the first stone of which was laid in 1566 by Charles IX.

Life in Paris was very different from his former existence. Maître Bernard was now the associate of men of science and art, with an acknowledged place in the Court circle. Under these new influences changes in design and decoration were made in the faïence in order to adapt it to this world of fashion. Scenes from famous paintings, allegorical subjects, and mythological heroes replace the fish and lizards and plants.

It was on August 24, 1572, the Eve of St. Bartholomew, that for the second time Palissy was saved from death because of his accomplishments in art. Catherine de Médicis sent him word not to leave his house that night. A little later he left Paris and traveled in Germany, the Rhine provinces, and Flanders. He studied fossils in Lorraine and Soissons; marne in La Brie; hot-springs in Aix-la-Chapelle. On the 24th of June, 1575, he returned to Paris. The journey had been rich in experiences and fruitful in material for future study. It was as scientist, rather than potter or Huguenot, that Maître Bernard returned to Paris.

From his study of the "beautiful book of Nature" Palissy had formed certain theories which he wished to publish, but first he wanted to discuss them with those who, from acquaintance with the classics, might have knowledge with which to contradict him. To this end he announced that he would give three lectures in which he would explain all he knew about springs, stones, metals, and their properties. The entrance fee was set at one écu. A four-fold return was promised in case it was shown that he had lured any there on false pretensions. "Thanks be to God," he says with considerable relief, "no one contradicted by a single word."

The lectures began in Lent, 1575, and were called by Maître Bernard, "My little Academy." It was the first scientific conference ever held in France. A distinguished assembly greeted him that spring day: noblemen, gentlemen, ecclesiastics, celebrated surgeons, lawyers, to mention only a few. The lectures were published in 1580 and were dedicated to Pons, at the time living in banishment in Rome in poor circumstances.

The solvent power of water was Maître Bernard's basic theory for the formation of the earth, whose rocks were disintegrated and salts dissolved and carried by the percolating waters to modify the quality of well and spring. The presumptuous claims of the alchemists he denounced, for in his opinion the creation and transmutation of metals are "tasks done by the command of God, invisibly and so secretly that man has no knowledge of the process." Crystallization is explained as a process due to

"affinity" or "attraction," something in the nature of a fifth element. Whatever it is, this unknown matter is found in all things and is the active force in salt, mineral, and plant formation. This was a generalization of the first order. Not perfectly accurate, it is true, but it must be remembered that Maître Bernard was using a language not yet adapted to scientific thought and that his handicap was very considerable.

From a study of fossils found in the vicinity of Paris, he concludes that "there had been in that place some great reservoir of water, which had contained an infinite number of fishes protected by shells like periwinkles. . . . Then after the water failed, the fish, the sand and mud, which they had inhabited, was hardened by the same congealing force that had destroyed the fish." In his essay on marl, agricultural chemistry and plant physiology are discussed. The essential constituent which gave to marl its peculiar value was, in Maître Bernard's opinion, the fifth element, "generative or congelative water."

This "congelative water" was an essential part of his theory. It shows the imaginative quality of his genius. There was much that he could not explain in natural phenomena. The great delusion of phlogiston of the seventeenth and eighteenth centuries illustrates the struggle of later scientists to find explanations for some of the natural phenomena which Palissy was also striving to explain. Only quantitative analyses based on mathematical precision were to clear up these difficulties. Bernard Palissy was far ahead of his century in his observations and deductions.

The lectures continued some ten years. Maître Bernard was recognized as a "philosopher of natural history, a man of keen and energetic mind." However, religious troubles were again disturbing the country and in 1587 Palissy was arrested and shut up in the Bastille. His release was secured by the Duc de Mayenne, but he was again arrested some two years later.

In the archives of the Prefecture, it is recorded that on "Monday the 4th of July, 1589, Bernard Palissy was hanged, strangled, and his body burned to a cinder. For his heresy was this done."

"He devoted his youth to his craft, his house to his art, his liberty and his life to his God. Such was Palissy!"

A COLORED AMMONIA FOUNTAIN

DORIS A. GRIFFOUL, PARKER HIGH SCHOOL, CLARENCE, NEW YORK

Try a few drops of phenolphthalein in the ammonia fountain. A pink fountain shows off to much better advantage than a colorless one, and has the additional advantage of illustrating the basic property of the ammonia.

INTRODUCTION TO SYMPOSIUM* ON "MATHEMATICS IN THE SERVICE OF CHEMISTRY"

FARRINGTON DANIELS, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

The object of this symposium is to further an appreciation of one of the chemist's most useful tools—mathematics. A few years ago we were still fighting for calculus for chemists, but that battle has been won and we are concerned here with higher mathematics and its application. Times are changing, as this program will show. We can see the mathematical physicist step in and solve our own problems more easily than we can solve them ourselves. Let the chemist who stopped growing in 1920 try to predict how fast a reaction will go; or give the chemical significance of an absorption or emission band; or tell how atoms are put together in molecules from the nature of the scattered light; or let him measure with precision the specific heat of oxygen up to 5000°. But these things are being done in 1931.

To actually do these things, the investigator must acquire a new vocabulary of wave equations, eigenfunctions, 1S-2P electrons, nuclear spin, etc.—but all sciences are shrouded in a mystery of technical terms. It is necessary, too, to travel a long, weary road of self-discipline and to solve thousands of problems. One cannot buy mathematical proficiency as he would buy a type K potentiometer. Many of us cannot afford, now, to take such a long road, but we can adopt a helpful attitude toward those who do and we can know where to go to solve some of our problems.

I have a letter of greeting addressed to this group from Professor E. R. Hedrick, president last year of the American Mathematical Society. Among other things he states that a Committee of the Social Science Research Council has asked that the Mathematical Society coöperate in making mathematics courses more helpful to students of the social sciences and that they include social science problems as well as engineering problems. I believe that we are negligent in this respect and that we should in some way ask for the special coöperation in elementary training which the mathematicians are willing to give. Somehow our chemists must be better trained in mathematics or we shall be completely outclassed by our chemist friends in Europe.

The time is coming and is now here when chemistry departments will

* This symposium was held under the auspices of the Division of Physical and Inorganic Chemistry of the A. C. S., on March 31, 1931, at Indianapolis, Indiana. In addition to the contributions included in this issue other papers in the symposium were as follows: R. H. FOWLER, "Statistical Mechanics"; W. H. RODEBUSH, "Calculation of Chemical Equilibrium from the Data of Band Spectroscopy"; R. S. MULLIKEN, "New Developments in Valence"; T. R. HOGNESS, "The Strength of the Carbon Bond"; D. S. VILLARS, "The Present Status of Polymolecular Band Spectroscopy"; HENRY EYRING, "Quantum Mechanical Calculation of Heats of Activation"; H. L. JOHNSTON, "The Specific Heats of Nitric Oxide and of Oxygen. The Precise Calculation of the Degree of Dissociation of Oxygen Up to 5000°."

have their professorships of mathematical chemistry. They are just as important as professorships of mathematical physics and more necessary. Most professors of physics are fairly good mathematicians and most professors of chemistry *are not.* Very shortly, too, we will have our consulting mathematicians who will help us, just as our consulting chemists now help the manufacturer and engineer.

The program is divided into four sections. You are all familiar with the help that mathematics has given through thermodynamics in predicting chemical equilibria. You may not be so fully aware that probability constitutes the backbone of our new advances, and that statistical mechanics is waiting to serve us in this field.

Quantum theory and atomic structure come next. Twenty years ago we were content to consider an atom as a hard round ball and to accept as unrelated and empirical, a whole mass of laboratory facts. With almost unbelievable speed we have crossed off from our list many of the so-called "specific properties of matter," making them functions of our new atomic models. To do this we have had to pay the price of complexity. In our evolutionary process we have accepted compressible atoms, then nests of square boxes, then elliptical orbits. Each has been more useful and more complicated than its predecessor. But now we have to abandon hope of expressing *all* our facts adequately with these simple pictures,* and we accept as inevitable, as complicated, but as useful—the new mathematical model.

* It is still necessary and useful to employ pictures and models but we have learned to take them less seriously. We have outgrown our three dimensions for we are concerned with more than three variables. Although it is impossible to represent *all* the properties with models in two or three dimensions, it is possible to represent *some* of them adequately and clearly with simple models. No one would think of giving up the benzene ring for a mathematical model in organic chemistry.

THERMODYNAMIC CALCULATIONS*

MERLE RANDALL, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

A standardized form of five simple thermodynamic equations is presented. By the intelligent use of these five equations more than ninety-five per cent of the thermodynamic problems usually encountered can be solved. A useful function, which includes the effect of heat capacity terms is considered. This function replaces log pressure as usually plotted against the reciprocal of the absolute temperature. The necessity of the correct formulation of the process and the validity of classical thermodynamics are discussed.

. . . . . .

We chemists are prone to consider ourselves superior creatures quite beyond the influence of fad or fancy. Yet, chemists have been known to become slaves to the fashion of the moment. These chemical fashions come and go. At first they arrive slowly, then autocatalytically they engulf the profession. Afterward, when the new theory or the new method has been assimilated into the body of our science the propagandists are forgotten. All is quiet, until a new fashion, which may make another name famous, becomes the rage of the season.

Thermodynamics has now passed the stage of mere fashionableness. Whether we be of those who purpose to ignore the practical usefulness of scientific study, or whether we see only the phrase, "The object of technical endeavor is profit," we seek its aid. Thermodynamics now needs no champion. Both theoretical and technical, if not practical, chemists are willing to accept the thermodynamic method. Yes, sometimes they invent near-thermodynamics with which to mystify themselves and others. For, as with every great scientific method, practices have arisen which cannot be justified, and which are even prohibited by the method itself.

It is my purpose, in the few brief minutes allotted to me, to show how easily the calculations necessary to translate tabulated data into usable information can be made. It will also be my purpose to point out a few common errors of calculation, interpretation, and application which have come to my attention. I shall also briefly consider the validity of our common fundamental equations.

The Mechanics of Thermodynamic Calculations

After the romantic period comes the period of standardization and of development. The actual mechanics of our chemical thermodynamic calculations have now been so standardized that with only five very simple equations we can make ninety-five per cent of our calculations. By

* Contribution to the symposium on "Mathematics in the Service of Chemistry," held under the auspices of the Division of Physical and Inorganic Chemistry, at the 81st meeting of the A. C. S., at Indianapolis, Indiana, March 31, 1931.

adhering to this standardized procedure we eliminate the possibility of those troublesome errors of sign with which the numerical application of thermodynamics has been beset.

Such calculations demand that we adhere rigorously to a convention, once that convention is adopted. It is much the same as with the rule of the road. A few are individualists, and insist on driving where they please, sometimes on the left and sometimes on the right. Some can get away with it, but when the traffic becomes too crowded or the pace too rapid they usually land in trouble. Thermodynamics has suffered all too much from the lack of a universally adopted system of conventions.

Before we can discuss a process we must define that process. This is most easily done by writing the process in the form of a chemical equation, which includes, besides the usual information as regards the stoichiometry, a statement of the state of the substances* entering into the reaction.

$$j\mathrm{J(s)} + l\mathrm{L(g,}\ P_\mathrm{L}\ \text{atmos.)} + m\mathrm{M}(m = m_\mathrm{M}) + \mathbf{N}\mathrm{E}^- + \ldots = r\mathrm{R(g,}\ P_\mathrm{R}\ \text{atmos.)} + s\mathrm{S}(m = m_\mathrm{S}) + t\mathrm{T}(\mathrm{N} = \mathrm{N_T}) + \ldots$$

Thus j mols of J at unit activity, l mols of L at P_L atmos., m mols of M at molality m_M, and $\mathbf{N}$ mols of electricity, etc., give r mols of R at P_R atmos., s mols of S at m_S molality, and t mols of T at mol fraction $\mathrm{N_T}$, etc.

The first and most important of the five most used thermodynamic equations is

$$\Delta F = 0 \text{ (the condition of equilibrium).} \tag{1}$$

If ΔF is positive, then the reaction will not proceed spontaneously from left to right, but if ΔF is negative, then the reaction may proceed spontaneously as written from left to right. That is, it will proceed provided the rate of the reaction is measurable.

Our second equation defines a quotient, known as the activity quotient Q, and enables us to calculate ΔF for any desired activities of the reacting substances, when the value of the standard free energy change, ΔF°, of the reaction is known.

$$\Delta F = \Delta F^\circ + RT\ln Q. \tag{2}$$

$$Q = \frac{a_\mathrm{R}^r\, a_\mathrm{S}^s\, a_\mathrm{T}^t \ldots}{a_\mathrm{J}^j\, a_\mathrm{L}^l\, a_\mathrm{M}^m \ldots} \tag{2a}$$

In exact calculations where the activity of a gas may not be equal to its partial pressure, or the activity of an aqueous solution or of an ion may not be equal to its molality, etc., the partial pressures, the molalities, etc., are multiplied by empirical numbers called activity coefficients. But for preliminary or approximate calculations the activity coefficients can be taken equal to unity, that is, the activity of the gas is taken equal to its partial pressure in atmospheres of an undissociated aqueous solution or

* See reference (*1*) for full discussion and the derivation of the equations of this paper.

of an ion equal to its molality, of a solvent equal to its mol fraction, and of solids or pure liquids as equal to unity.

The quantity ΔF° is a typical extensive quantity and is found at the standard temperature of 25°C. by adding algebraically the values of ΔF° of formation as found in the tables of free energy.

It is worthwhile to note that at equilibrium $\Delta F = 0$, and hence

$$\Delta F = 0 = \Delta F^\circ + RT\ln K, \quad \text{or} \quad \Delta F^\circ = -RT\ln K. \tag{2b}$$

The equilibrium constant, K, is merely the special value of Q when the system is at equilibrium. Referring back to equation 2, we also note that when the values of all the activities are unity, that is, all the substances taking part in the reaction are at their arbitrarily chosen standard states, the value of Q is also unity and the value of ΔF under these conditions is ΔF°, which indeed is the definition of ΔF°. It is a very common error to confuse Q and K, and also ΔF and ΔF°, an error, moreover, which leads to much confusion.

Our third equation defines the electromotive force of a cell or of a cell reaction in terms of the free energy. We define the sign of the electromotive force so that it also may be used as a criterion of equilibrium. If the electromotive force is zero, the reaction is at equilibrium, if it is positive, the reaction tends to proceed spontaneously, and if negative, the reaction will not spontaneously proceed from left to right as written. Thus,

$$\Delta F = -\mathbf{NEF}, \text{ (Faraday = 23,074 calories per volt equivalent).} \tag{3}$$

$$\mathbf{E} = \mathbf{E}^\circ - \frac{RT}{\mathbf{NF}}\ln Q \tag{3a}$$

or at 25°C.

$$\mathbf{E} = \mathbf{E}^\circ - (0.05915/\mathbf{N})\log Q. \tag{3b}$$

Defined in this way, the electromotive force is the free energy per equivalent, given the negative sign and placed in different units. If $\mathbf{E} = 0$, then as before the value of Q becomes K.

Our fourth equation gives the change of the standard free energy with the temperature. For convenience we tabulate the standard free energies of formation at 25°C. Thus, to work at any temperature, we first sum the free energies of formation to find the standard free energy change at 25°. Then by means of either of these equations we find the standard free energy change at the desired temperature. By the previous equations we can then find ΔF at the desired temperature for any desired values of the activities or Q.

$$\Delta F^\circ = \Delta H^\circ + IT \tag{4}$$

$$\Delta F^\circ = \Delta H_0^\circ - \Delta\Gamma_0 T\ln T - {}^1/_2\Delta\Gamma' T^2 - {}^1/_6\Delta\Gamma'' T^3 + \cdots + IT \tag{4a}$$

The first form of equation 4 assumes that the heat of the reaction does not vary with the temperature, and the second form assumes that the heat

capacities of the reacting substances can be expressed as algebraic functions of the temperature. This equation is really not so complicated as would appear at first sight.

Finally, we sometimes wish to know the entropy change in a reaction, or knowing the entropy change and either the increase in the free energy or heat content we may calculate the third quantity.

$$F - H = -TS, \quad \text{or} \quad \Delta F - \Delta H = -T\Delta S. \tag{5}$$

The five equations which I have given, will, when intelligently used, solve more than ninety-five per cent of the problems usually presented. They will solve a larger percentage of the technical problems. The solutions in this manner will present few numerical difficulties, will require a minimum of time, and will be free from those troublesome errors of sign which commonly cause one to lose confidence in results.

The Sigma Function

We are all familiar with the plot of vapor pressure against temperature. The curve is decidedly convex downward, and does not permit of easy interpolation or extrapolation. We are also familiar with the plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature. This plot is a straight line, the slope of which when multiplied by a constant gives the heat of vaporization or the heat of the reaction.

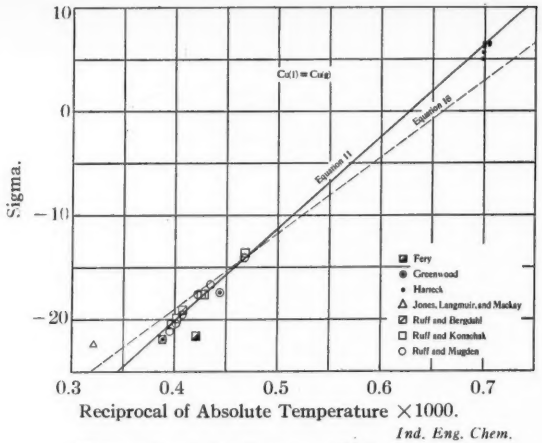
If we remember that at equilibrium $\Delta F^\circ = -RT\ln K$ and divide equation 4*a*, which is the most general form of the equation for the change in free energy with the temperature, by the absolute temperature and rearrange the terms, we have

$$\Sigma = -R\ln K + \Delta\Gamma_0 \ln T + {}^1/_2\Delta\Gamma' T + {}^1/_6\Delta\Gamma'' T^2 + \cdots = \Delta H_0^\circ/T + I. \tag{6}$$

If then sigma is plotted against the reciprocal of the absolute temperature we should have a straight line whose slope is ΔH_0° (the empirical heat of reaction at absolute zero) and whose intercept on the axis of $1/T$ is the thermodynamically indeterminate constant I. Such a plot is shown in Figure 1, which is for the vaporization of liquid copper.

The sigma function has proved most useful in correlating equilibrium data at various temperatures. The algebraic heat capacity terms are always taken from calorimetric data. It is not so important that these heat capacities be accurate as that, once chosen, they be retained and the same value be used in all calculations involving a particular substance. If the heat of the reaction is to be obtained from the equilibrium data alone, then the summation, sigma, becomes useful in calculating I.

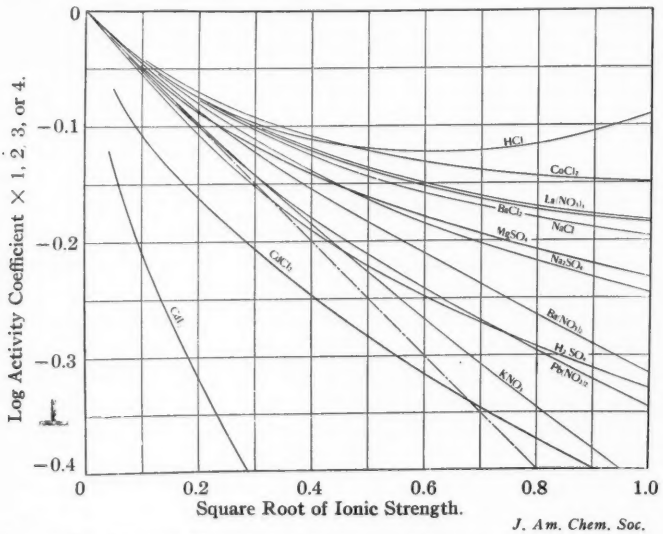
The accuracy in obtaining ΔH° by taking the slope as in Figure 1 is not high, but if we get an approximate value of ΔH_0° from the plot, we



Ind. Eng. Chem.

FIGURE 1.—SIGMA PLOT FOR Cu(l) = Cu(g)

can calculate an approximate value of I. If these approximate values of I are now plotted against the reciprocal of the absolute temperature, the slope of the best average straight line may be added to the original approximate value of $\Delta H_0°$ to obtain the best value of this constant. We may then calculate the true values of I, and the deviation of these individual



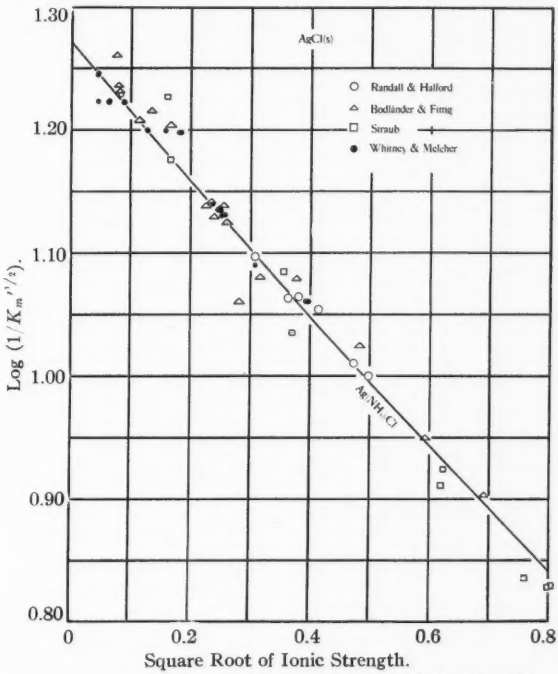
J. Am. Chem. Soc.

FIGURE 2.—ACTIVITY COEFFICIENT OF AQUEOUS SOLUTIONS OF ELECTROLYTES

values from the average value is the best criterion of the accuracy of the equilibrium data.

The Chemical Equation Must Represent the Process

From a strictly theoretical point of view thermodynamics does not inquire into the mechanism of a process. It is unnecessary to assume the existence of molecules, but from a practical standpoint the assumption of the existence of certain molecular species greatly simplifies our calcula-



J. Am. Chem. Soc.

FIGURE 3.—SOLUBILITY OF SILVER CHLORIDE IN AQUEOUS AMMONIUM HYDROXIDE AT 25°

tions. If we choose certain formulas for the various species taking part in the reaction, our thermodynamic deductions will agree with mechanisms which from extra-thermodynamic reasoning we believe to give a reasonable picture of the process.

As an example let us consider the solubility of silver chloride in aqueous ammonia, which may be assumed to take place according to the equation

$$AgCl(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + Cl^- + 2H_2O(l). \qquad (7)$$

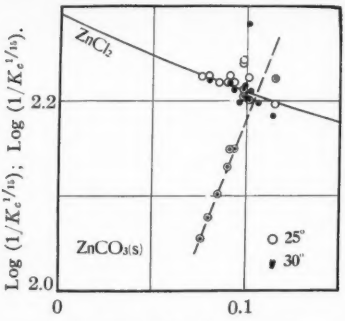


FIGURE 4.—SOLUBILITY OF ZINC CARBONATE IN AQUEOUS CARBONIC ACID

This determination may be made over a wide range of molalities of ammonia. The activity coefficients of the complex chloride would be expected to have values approximately the same as those of other uni-univalent substances. The formula $Ag(NH_3)_2^+$ is the only formula which will give the expected activity coefficients. Figure 2 shows some typical activity coefficients, those of the silver ammonia complex (*2*) shown in Figure 3 being much like those of potassium nitrate.

The formula of the solid phase in the determination of the solubility of zinc carbonate in aqueous carbonic acid was not given by the author (*3*). The solubility might have been represented by either of the equations

$$ZnCO_3(s) + H_2CO_3\ (aq.) = Zn^{++} + 2HCO_3^- \quad (8)$$

$$2ZnCO_3{\cdot}3Zn(OH)_2{\cdot}H_2O(s) + 8H_2CO_3(aq.) = 5Zn^{++} + 10HCO_3^- + 7H_2O(l). \quad (9)$$

The solid curve of Figure 4 shows the activity coefficients of zinc chloride superimposed upon a function proportional to the activity coefficients of aqueous zinc bicarbonate. With the formula $ZnCO_3$ we have the circles while with the basic formula we have the double circles. It is evident that the solid phase was the neutral zinc carbonate.

The Heat of Reaction as a Criterion of the Reaction

The heat of reaction as calculated from the equilibrium data must agree with the calorimetric value, else one must look for an error in the experimental data, a lack of attainment of equilibrium, or an error in the formulation of the process. In the case of the vaporization of mercury where the highest vapor pressure was 10^{11} times the lowest, the $\Delta H_0°$ calculated was constant over the entire range and agreed with the calorimetric value.

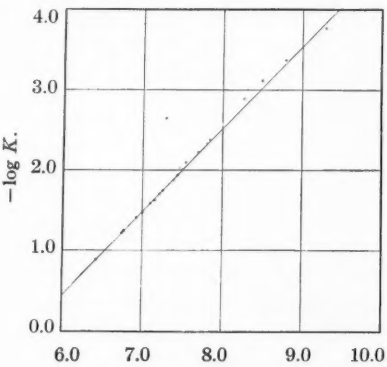


FIGURE 5.—DISSOCIATION OF DIATOMIC BROMINE GAS

$Br_2(g) = 2Br(g)$

In the case of the vaporization of liquid copper (Figure 1) there are no calorimetric data. But it is possible to calculate a theoretical value of the constant I, based upon a calculated increase in entropy in the reaction and the algebraic heat capacities. This value of I combined with the equilibrium data give a $\Delta H°$ represented by the dotted curve. There is some evidence that copper vapor is largely diatomic. Making this assumption, and estimating by the aid of spectroscopic data, a value for the entropy of diatomic copper we obtain better agreement between two such calculations, as were made for monoatomic copper vapor, than in the above case (*4*).

A beautiful confirmation of an assumed reaction is furnished by data for the dissociation of diatomic bromine gas. The points of Figure 5 are the experimental points of Bodenstein (*5*). By using a few of the most reliable points, those above 1400°K., to aid in calculating the moment of inertia of the diatomic molecule from spectroscopic data Gibson and Brown (*6*), in our laboratory, obtained the slope ($\Delta H°$) and the curvature of the curve shown in Figure 5 from spectroscopic measurements.

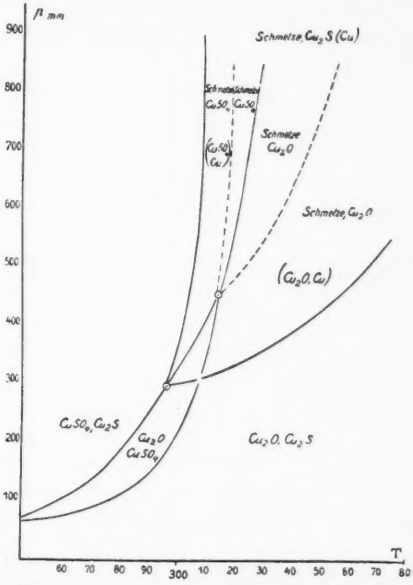


FIGURE 6.—PRESSURE-TEMPERATURE PLOT FOR SOME REACTIONS INVOLVING COPPER SULFATE, COPPER, SULFUR DIOXIDE, CUPROUS OXIDE AND SULFIDE

In Figure 6, I show the plot of the partial pressure of sulfur dioxide against temperature given by Schenck and Hempelmann (*7*) over solid phases containing various mixtures of cuprous oxide and sulfide, copper, copper sulfate, and cupric sulfide. They assumed a transition point at 300°. The measurements were partially confirmed by Reinders and Goudriaan (*8*), but they all neglected to test their explanations by the reasonableness of the heat of reaction corresponding to each of their curves. This figure also illustrates the difficulty in making any deductions from a direct plot of pressure against temperature. They must have made the common error that they had not attained equilibrium in their measurements. They must have had some sort of a steady state instead of an equilibrium.

When $-R\ln P$ is plotted against the reciprocal of the absolute temperature, as in Figure 7, the slope gives the heat of reaction per mol of sulfur dioxide evolved. In the case of their reaction

$$3Cu(s) + CuSO_4(s) = 2Cu_2O(s) + SO_2(g) \qquad (10)$$

the solid curve to the right from calorimetric data agrees with most of their experimental points. In the case of the second reaction

$$2CuSO_4(s) + Cu_2S(\beta) = 2Cu_2O(s) + 3SO_2(g) \qquad (11)$$

the solid curve to the left is from calorimetric data and from the accepted values for the free energy of formation of the reacting substances as given

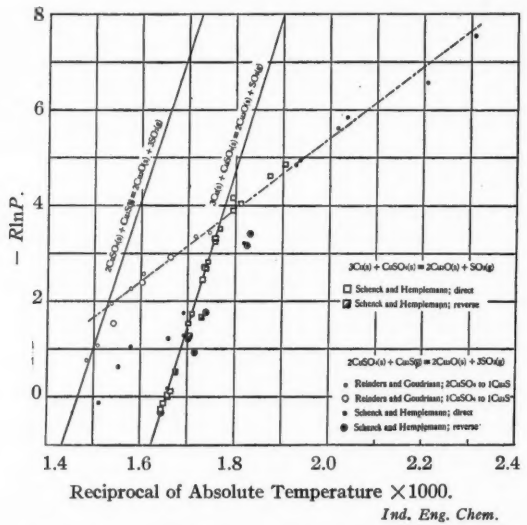


FIGURE 7.—$-R\ln P$ PLOT FOR SOME REACTIONS INVOLVING COPPER SULFATE, COPPER, SULFUR DIOXIDE, AND CUPROUS OXIDE AND SULFIDE

by Randall, Nielsen, and West (*4*). It is thus seen that only two of the experimental points fall near the curve. Yet this curve is a combination of other experimental data that seems reliable. We could draw straight lines through a series of these points but one of these would give a value of ΔH° only half the calorimetric, and another possible straight line would give a ΔH° only one-third the calorimetric. We were unable to find any assumed reaction which would give a ΔH° near the values corresponding to these low values from the plot. Evidently the pretty diagram of Figure 6 must be erroneous and their lines must represent either false equilibria or steady states.

Systems Not in Equilibrium

There have been numerous attempts recently to apply thermodynamic methods to systems not in equilibrium, especially in the cracking of petroleum products. Obviously, thermodynamics cannot predict the concentrations in such systems. We may, however, when adequate data are available concerning the activities of the particular substances present, say whether or not a particular reaction is possible. To be a possible reaction, or a possible side reaction, ΔF must be negative. But the speed of the reaction must also be finite, and thermodynamics does not predict speeds.

The Necessity of Consistency in the Tabulation of Data

The greatest utility of the thermodynamic method lies in the ability to correlate data obtained in a large variety of ways, and through various combinations of data from various reactions. Arithmetical accuracy, far greater than the accuracy of individual data will justify, is necessary so that when additions and subtractions of data are made the error may not be larger than that of the most accurate data. This means that it is far more important to continue to use a constant, or an arbitrarily chosen value of a property, rather than to combine a newer value of a constant with data which involve the old constant. The combinations of data are so intricate that this choice of constant cannot be left to the individual.

There was chaos in the field of stoichiometry until the International Committee on Atomic Weights was formed to decide upon consistent values for the atomic weights, which were to be used for definite periods of time. Revisions in the table of atomic weights are made in such a way as to maintain the maximum consistency in the mutual relations of these constants.

Our present tables of free energy rest upon constants chosen more than twenty years ago. It is my hope to perfect a plan by which these tables can be revised. The work must be centralized if it is to be done in the best way. Such a plan has been approved by the Division of Chemistry and Chemical Technology of the National Research Council. It only awaits the necessary funds, amounting to about $11,000.00 per year, to give us a continuing revision and interpretation of the vast body of thermodynamic data which is scattered through the literature.

The Validity of Classical Thermodynamics

Many scientists have been troubled because there does not exist a valid formulation of the second law of thermodynamics. Hence, a rigorous mathematical and logical proof of the second law is lacking. However, although admittedly invalid in some cases, it is an extremely accurate

approximation, for all those cases in which a large or moderately large number of particles are concerned.

I wish to give only an idea or so gleaned from Professor Gilbert N. Lewis' new "Generalized Thermodynamics," the manuscript of which Professor Lewis has kindly shown me, and by whose permission I can make the following announcement. Professor Lewis has succeeded in placing thermodynamics on an exact, rigorous, mathematical, and logical basis, deriving the laws corresponding to those of classical thermodynamics as well as the laws of fluctuations from a single postulate. This derivation is much simpler than the previous less rigorous derivations and should satisfy our logical desires and our pedagogic needs as well as give us the desired valid statement of the second law of thermodynamics.

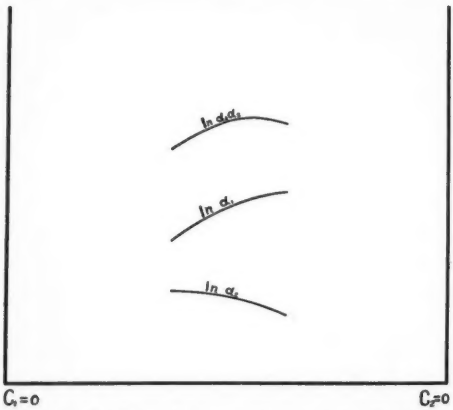


FIGURE 8.—THE LOGARITHM OF THE SPECIFIC PROBABILITY

Classical thermodynamics has attempted to give the definite answer, yes or no. It recognized just one equilibrium partition, which was not only the most probable partition, but also the average partition.

The new generalized thermodynamics gives us a quantitative answer. It tells us the probability that a system will be found in the most probable state. Figure 8 shows the logarithm of the specific probability that a given content C will be partitioned between two systems in a given manner. The center section is greatly enlarged. The specific probability, the product $\alpha_1\alpha_2$, belongs to a certain pair of contents C_1 and C_2. The partition represented by the highest point on the curve is the most probable equilibrium partition. Points on either side of the maximum represent the probability of other equilibrium partitions. These quantitative predictions become increasingly important as the number of particles in the system is decreased. Since we now have a valid statement of the second law, and since the usual laws of classical thermodynamics may be derived from the generalized thermodynamics, and are valid for our ordinary chemical systems composed of a moderately large number of particles, we may now use these fundamental laws with a new feeling of sureness.

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QUANTUM THEORY*

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The failure of Newtonian mechanics when applied to atomic systems, coupled with the observations on the scattering of photons by electrons and on the diffraction of electrons by crystal lattices, is adequately interpreted only on the basis of the new quantum mechanics. The Principle of Indeterminism is a logical consequence of these observations and leads to the interpretation of quantum mechanics as a statistical theory. The mathematical development of the theory has proceeded along two lines: the matrix mechanics of Heisenberg and the undulatory mechanics of Schrödinger. The former is discussed very briefly and the latter more fully, especially in regard to the significance of the mathematical technic. A brief discussion is given of the application of the Schrödinger theory to two simple problems and a comparison of the mode of treatment on the basis of quantum mechanics with that used in classical mechanics.

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Introductory Remarks

Just a little under fifty years ago Ostwald published his famous "Lehrbuch," and we are all familiar with the profound effect of this publication upon the subsequent development of chemistry. To chemists of the older school, the introduction into their field of the methods and concepts of physics and mathematics seemed the height of absurdity and nonsense. A new generation had to grow up before chemists could tolerate a partnership of chemical experimentation and calculus. It gradually came to be recognized that there exists a borderland of phenomena which may not be appropriated logically as a private preserve by either chemistry or physics, and that in this borderland, *viz.*, investigation of the phenomena due to atoms, molecules, and electrons, both chemists and physicists must be equally interested. The effect of this incorporation into chemistry of the point of view of the theoretical physicists has been a steadily growing attempt to interpret chemical phenomena by mathematical models of the same nature as those tested and found valid for physical phenomena. From a descriptive science, chemistry has tended more and more to develop into an exact science in which are utilized the ideals which had previously been stamped on physics from the time of Galileo and Newton.

For a time the chemist was able to follow these speculations of the theoretical physicists with more or less difficulty. The necessary mathematical equipment did not appear too mysterious for those with a little courage and will-power to investigate and understand; and, furthermore, the strain on the imagination was not so great but that the necessary mental

* Contribution to the symposium on "Mathematics in the Service of Chemistry," held under the auspices of the Division of Physical and Inorganic Chemistry, at the 81st meeting of the A. C. S., at Indianapolis, Indiana, March 31, 1931.

adjustment could be made fairly readily and we could say of an "explanation" that it had "explained." *Altera tempora, altera mores*—it would seem that we have now fallen upon evil days, for not only is there no explanation given of such a nature as those we have understood hitherto, but we are told by the theoretical physicists that "ye shall no longer worship any graven images or idols, nor shall ye make unto yourselves models that are tangible, for God is a pure mathematician and nature can never be interpreted in any other language than that of mathematics."

These recent developments constitute what is known as *quantum mechanics*. It is associated with the names of de Broglie, Heisenberg, Born, Schrödinger, Dirac, and others, and not only has it already caused a radical revision in certain fundamental concepts of physics, but also it has led to new points of view which are of the greatest significance for a more perfect understanding of such purely chemical problems as those of valency, catalysis, and chemical reactivity in general. The importance of these new views to physical chemistry has been emphasized in the presidential address to the American Chemical Society by Dr. I. Langmuir (*1*), and in the present connection I would like to quote from this address the following passage:

> Physics and chemistry are being inevitably drawn closer together. It seems that there has never been a time when we can predict with such certainty rapid progress in fundamental chemistry, for the new theories of physics have as yet scarcely begun to be applied in the field of chemistry. The physicist, on the other hand, has much to learn from an increased knowledge of chemical phenomena which should provide him with a richness of experimental data far greater than any he has yet had an opportunity to use.

To attempt an interpretation of this new theory in the brief space of time available for this address obviously requires a great deal of optimism. Much must necessarily be omitted, a great deal must be accepted by the audience on faith, and to the expert my remarks will appear as mere platitudes and a repetition of what he knows already. The speaker's qualifications for undertaking such a discourse are those of neither the theoretical physicist nor the mathematician, but of the layman who has tried to derive from the almost mystical symbolism of the philosophers, some understanding, dim though it may be, of the concepts involved and of the manner in which these are related to experimental observation. For after all, the *object of any scientific theory must be to develop a system of conceptions which will enable us to describe the results of an experience, or series of observations.* Or, as Dirac has stated it, "The only object of theoretical physics is to calculate results that can be compared with experiment, and it is quite unnecessary that any satisfying description of the whole phenomenon should be given." In scientific language the word "explains" indicates an answer not to the question "why," but to the more pertinent problem of "how" things happen.

Classical Quantum Theory

Quantum mechanics had its inception in 1900 when Planck formulated the hypothesis of energy quanta in order to account for the laws of blackbody radiation. This atomistic view of the nature of energy was emphasized by Einstein in 1905 in the statement that in the interaction of an atomic system or electron with radiation, the latter behaves as if constituted of light corpuscles or photons of magnitude $h\nu$, where h is Planck's constant and ν denotes the frequency of the radiation. By this corpuscular theory it was found possible to account quantitatively for the temperature variation of the specific heats of solids, for the photo-electric and inverse photo-electric effect, and finally for the Compton effect.

It is essential for a proper understanding of certain fundamental ideas of the new theory to describe more fully the last-named observations. When an X-ray impinges on matter, a secondary X-ray is produced of slightly longer wave length or lower frequency. This is contrary to what would be expected on the basis of the classical wave theory of light. In order to explain the phenomenon, A. H. Compton therefore suggested an interpretation based on the corpuscular theory.

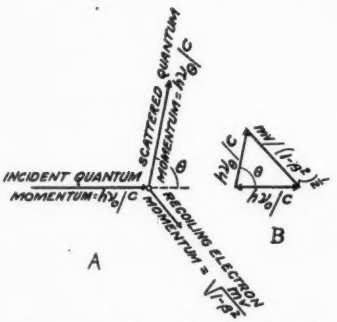


FIGURE 1.—(A), ILLUSTRATING THEORY OF COLLISION BETWEEN PHOTON AND ELECTRON (COMPTON EFFECT); (B), VECTOR DIAGRAM FOR MOMENTS OF PHOTON AND ELECTRON

On this theory the X-rays consist of a stream of energy quanta. While each photon carries the energy equivalent to $h\nu$, it also possesses the momentum $h\nu/c$ where c is the velocity of light. When the photon collides with a free or loosely bound electron, there occurs an interchange of both energy and momentum. Consequently, the photon suffers a recoil in one direction with loss of momentum, while the electron moves off in another direction with added momentum (see Figure 1). The decrease in momentum of the scattered X-ray photon corresponds to an increase in wave length, and Compton found that the actually observed changes in wave length were in agreement with the predictions based on the assumption of elastic collisions. A further point, brought out by subsequent experiments, is that this conservation of energy and momentum is not the result of a statistical state of affairs, but must hold valid for every individual collision between a photon and electron. Here, then, we have a phenomenon which must be recognized as indicating almost conclusively the corpuscular nature of radiation. Yet in these very

experiments Compton made use of the wave theory in the determination of the wave lengths of the primary and scattered radiation.

These and similar observations forced physicists to adopt a *dualistic conception of the nature of energy.* When dealing with interference, diffraction and polarization, we use the terms of the undulatory theory, that is, the wave length, λ, and wave velocity, $c = \nu\lambda$; when dealing with interaction of radiation and matter we speak of energy quanta, $h\nu$ and units of momentum, $h\nu/c = h/\lambda$.

The hypothesis of energy quanta was applied by Bohr to an interpretation of the origin of line spectra, and as the most important deduction from this theory there arose the concept of *discrete energy levels.* Whenever radiation is emitted or absorbed by an atomic system the frequency of this radiation is given by the well-known relation

$$\nu = (E_i - E_f)/h \tag{1}$$

where E_i and E_f represent the energy of the system in the initial and final states, respectively. These levels or stationary states were assumed by Bohr, in the case of at least the simpler spectra, to correspond to different possible orbits of the valence electron, and it was furthermore assumed that the laws governing the motion of the electrons in these orbits are those of ordinary or Newtonian mechanics. Since, however, it is possible according to classical mechanics to have a continuous variation in orbital constants corresponding to a continuous variation in total energy, it was necessary to postulate some sort of principle by which the possible number of orbits would be limited to correspond with the discrete energy levels deduced from spectral observation. Such a guiding principle or quantizing condition was first stated by Bohr in the form that in the case of a circular orbit the angular momentum of the electron must obey the relation

$$\mu v r = \frac{nh}{2\pi} \tag{2}$$

where μ = mass of electron, v = velocity, r = radius of orbit, and n = 1, 2, 3, etc.

The extension of Bohr's ideas by Sommerfeld and others led to a fairly consistent picture of atomic structures in which the more complex atoms could be regarded as being built up from elements of lower atomic number, N, by successive addition of electrons rotating in various elliptical and circular orbits. Furthermore, in order to define the "stationary states" of an atomic system, Sommerfeld and Wilson independently introduced the postulate that for any such state the total "action" taken over a complete period of revolution of the electron must be equal to an integral multiple, n_i of h. That is,

$$\oint p_i \, dq_i = n_i h \tag{3}$$

where q_i denotes one of the generalized coördinates, p_i the corresponding generalized momentum, and the integral is taken over a complete period of revolution. For each pair of variables, which correspond essentially to one of the positional coördinates (q_i) and the corresponding component of velocity (p_i), a quantum condition of the form just stated must apply. Also the experiments initiated by Franck and Hertz and continued by a number of American investigators, on the excitation and ionization of atoms by lines in the spectra of these atoms—all of these observations coming as direct consequences of Bohr's theory of energy levels—seemed to serve as a proof of the actual existence of electronic orbits.

However, when it came to the application of the laws of Newtonian mechanics to atomic systems containing more than one electron, difficulties of a more and more serious nature began to be encountered. For one thing, ordinary mechanics deals with continuously varying systems, and the existence of discrete energy states with quantum transitions presents a phenomenon totally foreign to the whole of classical theory. In the case of an electrical oscillator, the frequencies of radiation emitted are simple multiples of a fundamental, and the intensities of the individual monochromatic radiations are proportional to the squares of the amplitudes of the corresponding displacements in the motion of the oscillator. But in atomic systems, the frequency of emission of radiation bears no such simple relation to the frequency of rotation of the electron in its orbit, nor, in general, can the intensity of the light emitted be measured by any properties of a single orbit, since the radiation originates in a transition between two orbits. Under such conditions, how can one modify the laws of ordinary mechanics in order to obtain results in agreement with actual observations?

Bohr had recognized these difficulties early in the development of the theory, but he had pointed out that under certain conditions the deductions obtained by classical theory for macroscopic systems must be valid for atomic systems as well. It is well known that the laws of classical electrodynamics apply to radiation of long wave length; but such radiation is obtained, on the point of view of the Bohr theory, by transitions between orbits of very large radius, where the frequency of rotation is much smaller than for orbits of smaller radius—smaller values of the quantum number, n. For such large orbits, the frequency of the radiation emitted in passing from one orbit to a neighboring one is approximately equal to a simple multiple of the frequency of rotation in either orbit, and is therefore in accordance with classical theory. Hence the laws of ordinary mechanics may be applied to orbits of large quantum number, and the deductions thus obtained may then be extrapolated to the case of orbits of small quantum number. This idea, that in the limit the laws of quantum mechanics must approach asymptotically those of ordinary mechanics,

was formulated by Bohr as his famous *Correspondence Principle*, and it still furnishes the background for even the most recent developments in quantum mechanics. It will be observed that the essential purpose of this principle is to retain in atomic mechanics as much as possible of the classical mechanics which found its most important formulation in the so-called Hamiltonian canonical conditions and the Hamilton-Jacobi partial differential equation.

However, while this quantum mechanics, based as it was on a hybridization of ordinary mechanics and quantum discontinuities, gave quantitative results in the case of the normal hydrogen atom and ionized helium, it met with real difficulties in the treatment of the spectrum of neutral helium, where two electrons revolve around the nucleus. In the case of atoms of higher atomic number, the problem obviously becomes still more complex. Bohr attempted to deal with these atoms as perturbed states of the simple hydrogen-like system. By introducing the notion of penetrating and non-penetrating orbits, a certain measure of success was obtained in deriving a general form of expression similar to that which had been found to apply to spectroscopic terms. Also, by assigning to each electron in the atom four different kinds of quantum numbers, Sommerfeld, Landé, Pauli, Heisenberg, and others were able to develop semi-empirical formulas for the separation of multiplets and for the effects of magnetic and electric fields on spectral lines. In order to account for the absence of certain classes of transitions between levels, it was found necessary to postulate certain principles of selection regulating the nature of the possible transitions.

A further important generalization was derived by Pauli according to which "There cannot exist in any one atom two electrons having the four quantum numbers respectively the same for both." Utilizing this rule and the different selection principles, Hund was able to deduce a correlation between the arrangement and nature of the electrons in any atom, on the one hand, and the spectroscopic normal term on the other (*2*).

As stated already, all this development was based on more or less empirical considerations. All attempts to derive the same results by the methods of Newtonian or classical mechanics proved unsuccessful, and hence the question arose as to whether there is any reason whatever for expecting successful results by this method. Physicists like Bohr, Born, Heisenberg, and others began to consider the whole problem from a more fundamental point of view.

It was perceived that the failure to obtain satisfactory results by the application of Newtonian mechanics is due to the non-mechanical phenomenon of transitions with frequencies which do not correspond to those deduced for the orbital frequencies of revolution of the electrons. Furthermore, it was realized that the model of the Bohr theory involves

assumptions which cannot be justified under any consideration. As Born has stated it (*3*):

> The *true laws of nature are relations between magnitudes which must be fundamentally observable.* If magnitudes lacking this property occur in our theories, it is a symptom of something defective...In the case of atomic theory, we have certainly introduced, as fundamental constituents, magnitudes of very doubtful observability, as, for instance, the position, velocity, and period of the electron. What we really want to calculate by means of our theory and can be observed experimentally, are the energy levels and the emitted light frequencies derivable from them. The mean radius of the atom (atomic volume) is also an observable quantity which can be determined by the methods of the kinetic theory of gases or other analogous methods. On the other hand, no one has been able to give a method for the determination of the period of the electron in its orbit or even the position of the electron at a given instant. There seems to be no hope that this will ever become possible, for in order to determine lengths or times, measuring rods and clocks are required. The latter, however, consist themselves of atoms and therefore break down in the realm of atomic dimensions. It is necessary to see clearly the following points: all measurements of magnitudes of atomic order depend on indirect conclusions, but the latter carry weight only when their train of thought is consistent with itself and corresponds to a certain region of our experience. But this is precisely not the case for atomic structures such as we have considered so far.

Principle of Uncertainty

It was considerations such as these that led Heisenberg and Born in 1925 to suggest a theory of quantum mechanics based upon a radically new point of view. On the basis of this new theory Heisenberg was subsequently led to the deduction of a generalization which has been designated as the *Principle of Indeterminism or Principle of Uncertainty.* It postulates that in the case of atomic systems there exists a *fundamental limitation* governing the possibility of ever determining accurately both position and velocity of a corpuscle simultaneously.

In ordinary dynamics a particle of mass, m, moving with velocity, v, possesses a quantity of kinetic energy, $T = {}^1/_2\, mv^2$, and a quantity of momentum, $P = mv$. The force acting on the particle is defined in accordance with Newton's second law, by the rate of change of momentum, and a complete solution of the problem is obtained when we are able to derive the position of a particle at any given point and given instant of time *from a knowledge of the initial conditions and of the forces acting on the particle.*

This, however, assumes that the act of observing the motion does not of itself affect the motion. In other words, we postulate a system in a closed box, as it were, and then make observations on this system through a small opening in the box, assuming all the time that the system remains unaffected by the instruments which we use for making the observations. "However, in atomic physics," as Heisenberg (*4*) points out, "we may not make this assumption, since on account of the discontinuities in atomic

behavior, every interaction (between observer and system) can introduce relatively large changes of a partly uncontrollable nature."

As an illustration let us consider the measurement of the position of a moving electron at any instant. For this purpose we require a microscope of aperture Θ, as shown in Figure 2. With the electron moving in the direction of the x-axis, we illuminate the miscrocope slide with light of wave length, λ, incident from the direction indicated. From optical considerations, it is known that the inexactitude, Δx, in the determination of x, is given by

$$\Delta x = \frac{\lambda}{\operatorname{Sin}\Theta}$$

To make the observation it is necessary that at least one photon should be scattered by the electron and pass through the microscope lense into the eye of the observer. But in consequence of the Compton effect, the photon will lose momentum and will suffer recoil in a direction which cannot be controlled. The uncertainty in the magnitude of this loss in momentum in the x-direction is given by

$$\Delta p_x = \frac{h\nu}{c} \cdot \operatorname{Sin}\Theta = \frac{h}{\lambda}\operatorname{Sin}\Theta$$

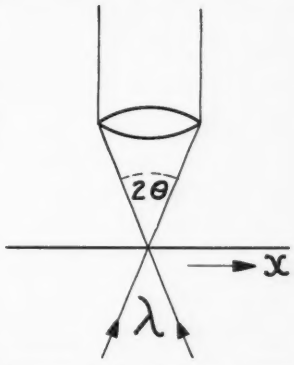


FIGURE 2.—ILLUSTRATING THE PRINCIPLE OF INDETERMINISM

Consequently, we have

$$\Delta x \cdot \Delta p_x = h. \qquad (4)$$

Also, we may attempt to measure the velocity (or momentum) of the electron by the Doppler effect on incident radiation of definite frequency. But in that case we shall find that, while to increase the exactness in the determination of p_x we must use very long wave lengths, we thereby decrease the degree of accuracy in determining position.

A similar relation is valid for the simultaneous determination of E, the energy, and t, the instant of observation. For in order to determine the difference in frequency, $\Delta\nu$, between two frequencies, ν and $\nu + \Delta\nu$, we must extend the observation over an interval of time $\Delta t = 1/\Delta\nu$. Hence

$$h \cdot \Delta\nu \cdot \Delta t = h$$

that is

$$\Delta E \cdot \Delta t = h \qquad (5)$$

Or, in order to determine the energy accurately, an infinite interval of time is necessary, and vice versa.

The significance of Heisenberg's generalization has been stated by Van Vleck (*5*) as follows:

When dealing with amounts of action comparable with Planck's h, one cannot assign accurate numerical values simultaneously to a coördinate and its corresponding momentum. Thus, within the atom, it is meaningless to talk of a simultaneous position and velocity of the electron. Experiments may be devised which will determine either x or p accurately, but not both x and p simultaneously. Instead, if Δx be the error in specifying the position x, and Δp that in specifying the momentum p, then the product $\Delta x \cdot \Delta p$ of the two errors is always of the order of magnitude of Planck's constant, so that

$$\Delta x \cdot \Delta p \sim h.$$

This is the so-called Heisenberg Indeterminism Principle, and, like the second law of thermodynamics, is very useful in predicting what experiments are possible, and what are inherently impossible. Thus high precision in position implies low precision in velocity, and vice versa.

Quantum Mechanics as a Statistical Theory

What then can we state about the calculation of orbits, orbital frequencies, etc., of electrons in atomic systems? Let us continue to quote from Van Vleck (*6*):

Because of the ambiguity resulting from the Heisenberg Indeterminism Principle, the future of a dynamical system can never be predicted with certainty. Instead only the *probability* that an electron be in a given configuration can be determined, and the future is only statistically determined. This is in sharp contrast to the "causality principle" of classical dynamics whereby the subsequent history of a dynamical system is determined if we know its initial coördinates and velocities. The uncertainty as to subsequent motion in quantum mechanics is, however, perhaps not due so much to failure of the ordinary cause and effect relation as to the inevitably indeterminate character of the initial conditions, as by the Heisenberg Indeterminism Principle one cannot give both the initial position and velocity accurately... *Thus quantum mechanics is essentially a means of calculating the probabilities of events.* In a laboratory experiment one performs certain operations and observes certain consequences. The goal of a theory must ever be to explain "what goes out" in terms of "what is put in." At first thought it may appear as if the purely statistical correlation between cause and effect demanded by quantum mechanics is contradictory to the precision with which experiments can be performed. Experiments with large-scale quantities, however, involve so many quanta that the Heisenberg Indeterminism is obscured, and so there is only apparently a "sharp" correlation. On the other hand, our ordinary atomic or molecular experiments are in most cases fundamentally statistical in character, as what is measured is not particular values of the dynamical variables, but rather *average values* of certain functions of these variables, or else *distributions* telling how they are scattered over a wide range of values. Such statistical quantities have a meaning in and can be calculated with quantum mechanics, and so there is no contradiction of Heisenberg's principle.

These conclusions are evidently quite at variance with those derived from classical mechanics. In the latter we are given a system for which the initial coördinates, (x,y,z) and corresponding momenta (p_x, p_y, p_z) are known definitely. Given the law of force, or potential energy function,

we can calculate by well-known methods of classical mechanics the exact values of both coördinates and momenta at any subsequent instant of time.

In quantum mechanics we can never determine both sets of variables simultaneously with the same degree of accuracy. The initial conditions are indeterminate to the extent defined by Heisenberg's principle. We can therefore calculate only the probability that at any given instant the system will be in a state, A, defined by certain coördinates, and also the probability that it will be in a state B defined by other coördinates. Hence, the concepts of orbit, orbital frequency, etc., disappear completely. Their place is now usurped by the concept of probability of occurrence at a given point, and it must be the object of quantum mechanics to calculate this probability as a function of the whole region of space. Thus in the case of the simple hydrogen atom, in the normal state, the electron according to the Bohr theory revolves in a circular orbit of radius $a_1 = 0.528 \times 10^{-8}$ cm. But according to quantum mechanics the electron may occur at any instant of time between the limits $r = 0$, and $r = \infty$. It is true that the actual calculation which is discussed subsequently shows that the probability of occurrence at even $r = 10a_1$ is vanishingly small, while it is a maximum for approximately $r = a_1$. Nevertheless this probability is never actually zero except for limits $r = \infty$ and $r = 0$.

It was these considerations which made it necessary to develop a new mechanics which should enable us to calculate these probabilities of occurrence and probabilities of transitions (which give a measure of spectral intensities) for atomic systems. Since, however, ordinary mechanics evidently yields correct results for large-scale phenomena we must demand of any new formulation of mechanics that *its deductions shall approach those obtained by Newtonian mechanics asymptotically as the quantum number is increased.* That is, for cases in which the quantum of action, h, becomes negligibly small ($h \longrightarrow 0$) the probability of occurrence must tend to become infinitely great for a more and more sharply limited region until finally it becomes equivalent to classical certainty for a definite orbit.

While the arguments stated so far for the new theory are based essentially on the experimental observations of the Compton effect, and the failure of classical mechanics in accounting for quantum phenomena, another line of reasoning based on the demonstrated wave nature of electron diffraction phenomena (discussed in a subsequent section) also leads to the same conclusions. As a consequence, the early development of the new quantum mechanics proceeded along two directions which, while regarded at the beginning as quite different, were subsequently shown to be mathematically equivalent. The first development historically was that initiated by Heisenberg and elaborated by him along with Born, Jordan, and Pauli. The formal mathematical procedure used by these investigators has been designated the *matrix mechanics.* The

second development, due to Schrödinger, and based on the wave concept of matter, makes use of methods which are similar to those previously used in solving problems of wave motion in general and is known as *wave mechanics*. More recently Dirac has formulated a treatment of quantum mechanics which is even more general than either the Heisenberg or Schrödinger method and which involves the latter as special "representations" in transformation of vectors.

To the student of classical physics the Schrödinger method appears the least difficult to follow. The notion of waves, even if it represents a convenient fiction, somehow furnishes a bridge, by means of which one may cross from the realm of familiar classical physics into that nebulous region of symbols and equations which constitute the new quantum mechanics. Nevertheless, it must not be forgotten that even the wave mechanics is a symbolic mode of treatment which is merely a variation, mathematically, of the Heisenberg and Dirac methods.

In the following discussion it is, of course, impossible to deal with these different aspects at all comprehensively. But perhaps it may be possible to convey to the reader some understanding, dim though it may be, of these new concepts on which the quantum mechanics is based.

Matrix Calculus

The matrix calculus may be crudely described as a type of algebra which enables us to solve an infinite number of simultaneous equations. It makes use of methods which have been studied by mathematicians since the time of Cayley and the rules of calculation are similar in many respects to those used in working with determinants.

In the Newtonian mechanics the problem of a single particle moving along one coördinate is formulated as a relation between the total energy, E, and the kinetic and potential energies (T and V, respectively) thus:

$$T = \frac{1}{2}\mu v^2 = \frac{(\mu v)^2}{2\mu} = \frac{p^2}{2\mu}$$

$$V = V(q)$$

$$E = T + V = \frac{p^2}{2\mu} + V \qquad (6)$$

where q represents the coördinate and p the corresponding momentum, while V is some function of q.

Thus, in the case of the linear harmonic oscillator, the relation is of the form

$$E = H = \frac{p^2}{2\mu} + \frac{kq^2}{2} \qquad (7)$$

where the restoring force is $-kq$ and H denotes the total energy expressed in the Hamiltonian form, that is, as a function of q's and p's.

Writing equation (7) in the form

$$E = \frac{m}{2}\left(\frac{dq}{dt}\right)^2 + \frac{k}{2}q^2$$

the result of integration leads to the solution

$$q = q_0 \text{ Sin } (2\pi\nu_0 t + \delta) \tag{8}$$

where

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}, \tag{9}$$

$$q_0 = \text{maximum amplitude} = \sqrt{\frac{2E}{k}} = \frac{1}{\pi\nu_0}\sqrt{\frac{E}{2m}}, \tag{10}$$

and δ is an integration constant which may be neglected for present purposes.

If now we introduce the quantum condition in the form

$$2\int_{-q_0}^{q_0} p\,dq = nh$$

where n is an integer, we obtain the result

$$E = nh\nu_0 \tag{11}$$

which defines the energy states of the oscillator.

In matrix mechanics we replace the coördinate q by an array of terms arranged in rows and columns, each term corresponding to a fictitious amplitude of the form

$$q(mn)\epsilon^{2\pi i\nu(mn)t}$$

where

$$\nu(mn) = (E_m - E_n)/h$$

and m and n designate, respectively, the *row* and *column* in which the element occurs.

From this array or matrix we can form a matrix q^2 in which the element in the mth row and nth column is formed by the multiplication of each number in the mth row of the first matrix by a corresponding number in the nth column of the second matrix and adding the products. Thus the element $a(mn)$ in the q^2 matrix is given by

$$\begin{aligned} a(mn) &= \sum_k q(mk)\epsilon^{2\pi i\nu(mk)t}\cdot q(kn)\epsilon^{2\pi i\nu(kn)t} \\ &= \sum_k q(mk)q(kn)\epsilon^{2\pi i\nu(mn)t} \end{aligned}$$

$$\left.\begin{aligned} \text{Since } \nu_{mk} + \nu_{kn} &= (E_m - E_k + E_k - E_n)/h \\ &= (E_m - E_n)/h \\ &= \nu_{mn} \end{aligned}\right\} \tag{12}$$

Similarly we form a matrix for p, of which the element is given by

$$\begin{aligned} p(mn) &= \dot{q}(mn) \\ &= 2\pi i\nu(mn)q(mn)\epsilon^{2\pi i\nu(mn)t} \end{aligned}$$

Now we form the matrix corresponding to

$$E = \frac{p^2}{2\mu} + 2\pi^2\nu_0^2\mu q^2$$

by adding the matrices corresponding to p^2 and q^2, and introduce the quantum condition in the form

$$\sum_k p(mk)q(kn) - q(mk)p(kn) = \frac{h}{2\pi i} \qquad (13)$$

while the matrix corresponding to E is a diagonal matrix, since all terms involving ν disappear.

From the relation between the matrix elements thus obtained, it is deduced that

$$E_n = (n + 1/2)h\nu_0$$

It will be recognized that this method of calculation does not lend itself to any physical interpretation. It is a *modus operandi* which works successfully because the rules are specially adapted for incorporating both the uncertainty principle, of which equation (13) may be described as a corollary, and also the Ritz combination principle of spectral terms, which is described by equation (12). Finally, mention should be made of the fact that in solving the matrices to obtain numerical results use is made of the classical Bohr correspondence principle, which states that for very large quantum numbers the results obtained must approach asymptotically those derived from Newtonian mechanics (that is, for $h \longrightarrow 0$).

The variables, p, q, and E, which correspond to real observable magnitudes in classical theory thus appear in the matrix mechanics as shadows of physical magnitudes, belonging to two different worlds, as it were, of which only one can be viewed distinctly under any given conditions, while the other must remain wrapped in a haze. The very fact that the p's and q's obey the non-commutative relation (13) shows, as Van Vleck states, the irrationality of any physical interpretation and "$\frac{h}{2\pi i}$ may be regarded as a measure of this irrationality."

A mathematician recognizes in the matrix calculus rules for carrying out certain kinds of transformations of vectors in a configurational space of an infinite number of dimensions. Thus a matrix may be regarded as an *operator*, and, in fact, equation (13) may be derived on this point of view by the following method:

Let us define the "observable" p_k as an operator of the form

$$p_k = \frac{h}{2\pi i}\frac{\partial}{\partial q_k}$$

Therefore

$$p_k q_k = \frac{h}{2\pi i} \frac{\partial}{\partial q_k} (q_k) = \frac{h}{2\pi i}$$

while

$$q_k p_k = q_k \cdot \frac{h}{2\pi i} \frac{\partial}{\partial q_k} (1) = 0$$

Hence equation (13) follows directly and it is this relation which takes the place of the Wilson-Sommerfeld quantum condition in the new theory.

De Broglie's Relation

While the methods of the matrix calculus are purely symbolical and far removed from the type of mathematics already familiar to theoretical physics, it was shown by Schrödinger, as stated already, that the results of the matrix calculus may be obtained, also, by use of partial differential equations of a type similar to those which have been utilized in the study of wave motion, theories of potential, heat conduction, and similar problems. Although the treatment by this so-called wave mechanics appears at first glance quite different from that adopted in the matrix calculus, it has been demonstrated by Schrödinger himself and others that the two methods are essentially equivalent mathematically and that the matrix elements may be calculated readily from the solutions of the Schrödinger partial differential equations.

The actual stimulus to this development of quantum mechanics was derived by Schrödinger from certain theoretical speculations of Louis de Broglie regarding the analogy between the laws of geometrical optics and those of classical dynamics.

As is well known, the laws of geometrical optics are more and more valid the shorter the wave length of light. For light waves comparable in length with those of the object upon which they impinge, that is, for rays having a radius of curvature comparable with the wave length, we must interpret the observations from the point of view of the undulatory theory. This suggested to de Broglie that probably Newtonian dynamics is also an approximation which is valid for macroscopic systems, but not for atomic systems because the radius of curvature of the electronic orbit is of the same magnitude as the wave length associated with the corpuscular motion.

Let us consider, for instance, the Bohr orbit of the electron in the normal state of the hydrogen atom. The quantum condition [equation (2)] leads in this case to the relation (since $n = 1$)

$$mvr = \frac{h}{2\pi}$$

where v denotes the velocity of the electron in a circular orbit of radius, r. If there is a wave length, λ, associated with this motion, the circumference

of the orbit must be an integral multiple of λ, and for the simplest case this multiple will be unity.

Hence $$2\pi r = \lambda.$$

Comparing these two equations it follows that

$$\lambda = \frac{h}{mv} \tag{14a}$$

which is the famous *de Broglie relation.* Since mv corresponds to the momentum (p), this relation may be written in the form

$$\lambda = h/p \tag{14b}$$

To obtain the frequency of this wave motion, de Broglie utilizes Planck's relation $E = h\nu$, where the total energy must be expressed on the basis of the theory of relativity in the form,

$$\left.\begin{aligned} E &= \frac{m_0c^2}{\sqrt{1 - v^2/c^2}} \\ &= mc^2 \end{aligned}\right\}$$

where m_0 and m denote, respectively, the value of the mass, for zero velocity and for velocity, v, which is small compared with that of light, c.

Hence the phase velocity or velocity of the individual waves is given by

$$u = \nu\lambda = \frac{E}{h} \cdot \frac{h}{mv} = \frac{mc^2}{mv} = \frac{c^2}{v} \tag{15}$$

Before discussing the significance of this relation, let us consider what values of λ we can expect, on the basis of de Broglie's theory for certain cases of corpuscular motion. The value of h as determined by different methods is 6.55×10^{-27} erg. sec. Hence for a mass of 1 g. moving with a velocity of 1 cm. per second, the associated wave length is 6.55×10^{-27} cm. This is certainly a value much too small to be measured by any sort of grating available. From the study of X-rays we know that it is possible by means of crystal lattices to measure wave lengths ranging from 10^{-10} to 10^{-7} cm., while optically ruled gratings enable us to measure wave lengths exceeding 10^{-6} cm. Thus, if de Broglie's assumption is valid, we would expect to find that corpuscular motion will exhibit phenomena of the same nature as those previously associated with light waves under those conditions where the momenta of the particles are of the order of magnitude $mv = h/10^{-10}$ to $mv = h/10^{-7}$, namely, for values of mv ranging from 6.55×10^{-17} to 6.55×10^{-20}. The magnitude of these values shows that we can expect such phenomena only in the case of atoms or electrons. Thus, according to the kinetic theory of gases, a hydrogen molecule ($m = 3.3 \times 10^{-24}$) has a velocity of about 2×10^5 cm. sec.$^{-1}$ at room temperature. The value of mv is therefore 6.6×10^{-19} which is within the range just mentioned. An electron falling through a potential of 100 volts acquires a velocity of 5.9×10^8 cm. sec.$^{-1}$ Multi-

plying by the mass ($m = 9 \times 10^{-28}$), we obtain the result $mv = 5.3 \times 10^{-19}$ and $\lambda = 1.24 \times 10^{-8}$ cm. For cathode rays of 25,000 volt velocity, λ calculated in the same manner is 0.75×10^{-9} cm. approximately.

Thus we might expect to find in the case of atoms and electrons certain phenomena exhibiting the characteristics ordinarily associated with waves, and incidentally this would be an argument for de Broglie's postulate that for such particles it is no longer justifiable to expect exact results by application of Newtonian mechanics.

Now as has happened in the history of science many times, the observations confirming this view became available shortly after the publication of the work of de Broglie and Schrödinger. This experimental evidence of the wave nature of matter was obtained by two physicists, C. Davisson and L. Germer, in the Bell Telephone Laboratories. They observed that electrons of moderate velocities (20 to 200 volts) impinging on a single crystal of nickel are reflected more frequently in certain favored directions, depending upon the velocity of the electrons and upon the distance between the atomic layers in the crystal lattice which happen to be normal to the plane containing both the incident and reflected electron beams. Applying the same relations as had been used by Bragg to determine the wave lengths of X-rays diffracted by a crystal lattice, Davisson and Germer found for the diffracted electrons values of λ in accordance with de Broglie's relation.

Furthermore, in England, G. P. Thomson actually sent high-velocity electrons (15,000 to 30,000 volts) through thin metal foils and obtained on a photographic film diffraction patterns of exactly the same appearance as those obtained by Laue in his classical demonstration of the wave nature of X-rays. G. P. Thomson merely applied the formula which had been used for X-rays to the diffraction of electron beams by the metal foil and obtained values of λ which were, again, in exact agreement with de Broglie's relation.

It is indeed a dramatic feature of recent developments in physics that the same methods which had been used to demonstrate, without shadow of a doubt, the undulatory nature of X-rays, which, on the other hand, in the Compton effect, inverse photo-electric effect, and ionization effect, exhibit corpuscular phenomena—that these same methods should have been used for the same purpose in connection with rays (electron beams) which had hitherto been considered as *prima facie* corpuscular. For what could be more justly regarded as a corpuscle than the infinitesimal electron whose charge and mass had been determined by J. J. Thomson by recognized electrodynamical laws?

More recently evidence has been obtained that beams of atoms of hydrogen and other gases reflected from crystal surfaces also exhibit phenomena which may be interpreted from the undulatory point of view.

We are thus confronted with the striking fact that electrons (or atoms) as well as photons are guided by waves. The dualistic concept of the nature of energy is found to be equally valid for electrons and material particles. As Dirac (7) describes these observations—

> *All* particles are connected in this way with waves, which control them and give rise to interference and diffraction phenomena under suitable conditions. The influence of waves on the motion of the particles is less noticeable the more massive the particles and only in the case of photons, the lightest of all particles, is it easily demonstrated.
>
> The waves and particles should be regarded as two abstractions which are useful for describing the same physical reality. One must not picture this reality as containing both the waves and particles together and try to construct a mechanism, acting according to classical laws, which shall correctly describe their connection and account for the motion of the particles...What quantum mechanics does is to try to formulate the underlying laws in such a way that one can determine from them without ambiguity what will happen under any given experimental conditions.

Wave Mechanics as a Statistical Theory

We must now consider the manner in which this association of wave motion and corpuscular dynamics leads to the Uncertainty Principle and to the consequent deduction that wave mechanics can enable us to calculate only probabilities, and not "orbits."

For a particle having momentum $p = mv$, the de Broglie relation associates a monochromatic wave motion of wave length $\lambda = h/p$, and velocity $u = E/p = c^2/v$. [See equation (15).] The very fact that this velocity exceeds that of light, and may even become imaginary on occasion (as will be shown subsequently), shows that this phase-velocity cannot correspond to the rate at which energy is transferred. The latter is given by the dynamical velocity, v, of the particle itself, with which the energy is associated. But if we try to assign an instantaneous position to the particle we find this impossible since in a monochromatic wave extending from $-\infty$ to $+\infty$ all points have an equal claim. That is, we have lost completely any indication of the location of the particle at any instant; in other words, exact knowledge of the momentum precludes any information whatever about the position.

To obtain the latter we must combine a group of waves, ranging in wave length from λ to $\lambda + \Delta\lambda$. These will combine to form a crest extending over a region x to $x + \Delta x$ at any instant and traveling with the so-called *group velocity* which is different from that of the individual waves (phase velocity) and may be shown to be identical with the velocity of the particle, v. The exactness with which it is possible to define the position of the particle is therefore limited by the extension in space of the crest of the group of waves. The greater the range of frequencies (ν to $\nu + \Delta\nu$) which we use in order to form the group, the narrower the extension in space, Δx, and, therefore, the more sharply may the *position*

be defined. But this means that in order to define the position accurately we must give up all idea of determining simultaneously, with a similar degree of accuracy, the *velocity* (or momentum). The relation is evidently of *a reciprocal nature*, and we have thus derived the conclusion stated previously in the Heisenberg Uncertainty Principle.

The more precise statement of this principle follows readily from the following considerations. The extent, Δx, of a group of waves of range λ to $\lambda + \Delta\lambda$ reinforce each other is given by

$$\Delta x = \frac{\lambda}{\Delta\lambda}\lambda$$

Therefore

$$\Delta x \cdot \frac{\Delta\lambda}{\lambda^2} = \Delta x \cdot \Delta\frac{1}{\lambda} = 1$$

and from de Broglie's relation it follows that

$$\Delta x \cdot \Delta\left(\frac{p}{h}\right) = 1$$

that is,

$$\Delta x \cdot \Delta p = h \tag{4}$$

Thus, as Bohr has pointed out, the Uncertainty Principle which Heisenberg deduced from a consideration of the limitations on observation set by the Compton effect and similar phenomena, follows just as naturally from the Davisson-Germer experiments and their interpretation, in terms of de Broglie waves associated with particles in motion.

All this indicates, according to Schrödinger, that for the consideration of atomic systems we must devise a system of dynamics which shall take into account the undulatory nature of corpuscular motion and thus lead to the calculation of certain statistical probabilities.

Now for any so-called conservative system, the relation is valid of the form

$$E = \frac{1}{2}mv^2 + V \tag{16}$$

where E is the total energy (which is constant) and V denotes the potential energy. The latter is ordinarily expressed as a function of the coördinates only. From equation (16) it follows that the momentum

$$p = mv = \sqrt{2m(E - V)} \tag{17}$$

is also a function of the coördinates. Thus the wave length and phase velocity, which is given according to equation (15) by the relation,

$$u = \frac{E}{\sqrt{2m(E - V)}} \tag{18}$$

vary from point to point in space, and we may replace the dynamical path of the particle by a wave front for which the direction of the normal

at any point is identical with that of the corpuscular motion. In this manner the problem of the behavior of a system for which the total and potential energies are defined by equation (16) becomes a problem of investigating the motion of a wave front in a region in which the velocity (or refractive index) varies from point to point, according to a law defined by equation (18).

Differential Equation for Wave Motion

Let us consider the simplest type of wave motion defined by the equation

$$y = A \operatorname{Cos} 2\pi \left(\frac{x}{\lambda} - \nu t\right) \tag{19}$$

where y denotes the *amplitude* as a function of a single coördinate, x, and of the time, t. It is evident that for a given value of t, y assumes the same value for $x = 0$, $x = \lambda$, $x = 2\lambda$, etc.; also for a given value of x, y is periodic in time with period $1/\nu$. The velocity of the wave motion is given by $u = \nu\lambda$.

From equation (19) it is seen that

$$\frac{\partial y}{\partial x} = -\frac{2\pi}{\lambda} A \operatorname{Sin} 2\pi \left(\frac{x}{\lambda} - \nu t\right)$$

$$\frac{\partial^2 y}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} A \operatorname{Cos} 2\pi \left(\frac{x}{\lambda} - \nu t\right)$$

$$= -\frac{4\pi^2}{\lambda^2} y \tag{20}$$

Similarly

$$\frac{\partial^2 y}{\partial t^2} = -4\pi^2\nu^2 y \tag{21}$$

Therefore

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{\nu^2\lambda^2} \cdot \frac{\partial^2 y}{\partial t^2} = \frac{1}{u^2} \frac{\partial^2 y}{\partial t^2} \tag{22}$$

This is the partial differential equation P. D. E. for a wave motion along one coördinate, and obviously equation (19) is one solution of the equation. Equation (22) is ordinarily derived directly by considering the transverse vibration of the element of a string of linear density ρ subjected to a tension T, in which case the resulting partial differential equation contains T/ρ for u^2, and the problem then arises of solving a partial differential equation P. D. E. of this form.

The classical method of solution involves as the first step the transformation of the equation into such a form that terms can be grouped according to the variables. This is known technically as *solution by separation of the variables*, and in the case of equation (22) it is seen that the right- and left-hand terms are of this nature, provided u is a constant. In that case we assume

$$y = f(x) \cdot g(t) \tag{23}$$

and by differentiating this, and substituting in (22) we obtain the relation

$$f''(x)\cdot g(t) = \frac{1}{u^2} f(x)\cdot \ddot{g}(t)$$

where

$$f''(x) = \partial^2 f/\partial x^2;\ \ddot{g}(t) = \partial^2 g/\partial t^2$$

Dividing through by $f(x)\cdot g(t)$, we obtain the relation

$$\frac{f''(x)}{f(x)} = \frac{1}{u^2}\frac{\ddot{g}(t)}{g(t)} \tag{24}$$

Since the left-hand side is independent of t, while the right-hand side does not involve x, we can equate each term to an arbitrary constant which we will designate by $-m^2$ (to indicate its negative value).

We thus obtain *two ordinary differential equations*

$$f''(x) + m^2 f(x) = 0 \tag{25}$$
$$g(t) + m^2 u^2 g(t) = 0 \tag{26}$$

The solutions of these equations are of the form:

$$\begin{aligned} f(x) &= A_0\epsilon^{+imx} + B_0\epsilon^{-imx} \\ \ddot{g}(t) &= C_0\epsilon^{+imut} + D_0\epsilon^{-imut} \end{aligned} \tag{27}$$

where A_0, B_0, C_0, and D_0 are arbitrary constants.

These may be expressed in the sine or cosine form by de Moivre's relations,

$$\begin{aligned} \epsilon^{ix} &= \operatorname{Cos} x + i \operatorname{Sin} x \\ \epsilon^{-ix} &= \operatorname{Cos} x - i \operatorname{Sin} x \end{aligned} \tag{28}$$

Therefore we can write the solutions in the form

$$f(x) = A \operatorname{Cos} mx + B \operatorname{Sin} mx \tag{29}$$
$$g(t) = C \operatorname{Cos} mut + D \operatorname{Sin} mut \tag{30}$$

where A, B, C, and D are arbitrary constants related to the constants in equations (27).

Equations (29) and (30) constitute the most general form of the solution of equation (22), but the constants A, B, C, D, and m require a physical interpretation. It is of course evident that actually only *two arbitrary constants* are involved in equation (29), *viz.*, A/B and m, for the product of $f(x)$ with any arbitrary constant will also be a solution of the differential equation (25).

For the determination of these constants, it is necessary to consider the nature of the *initial* and *boundary* conditions of the problem. Thus, in the case of a vibrating string of length L, fixed at both ends, the amplitude of vibration is zero at these ends. Hence

$$y = 0 \text{ for } x = 0 \text{ and } x = L$$

Since $\operatorname{Cos}(0) = 1$, this indicates that $A = 0$, and therefore $f(x) = B \operatorname{Sin} mx$.

To fulfil the condition

$$B \text{ Sin } (mL) = 0$$

we must have $mL = k\pi$, where $k = 1, 2, 3$, etc., that is

$$m = \frac{k\pi}{L} \tag{31}$$

We have thus found that equation (29) has a physical interpretation only for those discrete values of m which are defined by (31). These are known as *characteristic values* or *eigenwerte* and the corresponding values of

$$f(x) = \text{Sin } \frac{k\pi x}{L} \tag{32}$$

are known as *characteristic functions* or *eigenfunctions*. The constant B has been omitted in the last equation because the actual value depends upon the total energy of vibration.

It is evident from the nature of the sine or cosine function that L/k must correspond to $\lambda/2$ where λ is the wave length, and that therefore

$$m = \frac{2k\pi}{\lambda} \tag{33}$$

Substituting this in equation (30) we obtain the relation

$$g(t) = C \text{ Cos } \frac{2k\pi}{\lambda} ut + D \text{ Sin } \frac{2k\pi}{\lambda} ut.$$

If now we assume that for $t = 0$, $g(t) = 0$, we obtain the solution

$$g(t) = \text{Sin } \frac{2k\pi}{\lambda} ut.$$

and $g(t)$ will become zero for every value of t which is equal to $\tau/2$ where $\tau = 1/\nu$, denotes the period of vibration. Thus,

$$g(t) = \text{Sin } mut = \text{Sin } 2k\pi\nu t$$

that is,

$$mu = 2k\pi\nu \tag{34}$$

gives the eigenvalues of equation (30).

From (33) and (34) it follows that $u = \nu\lambda$ and that consequently u is the velocity of the wave motion. The complete solution of the partial differential equation for the given initial and boundary conditions is therefore

$$\begin{aligned} y &= \text{Sin } \frac{k\pi x}{L} \text{ Sin } \frac{k\pi ut}{L} \\ &= \text{Sin } \frac{2\pi kx}{\lambda} \text{ Sin } (2\pi k\nu t) \end{aligned} \tag{35}$$

where $L = \lambda/2$; $\nu = u/\lambda$.

Schrödinger Equation for One Coördinate

Again we consider the P. D. E. (22) but shall replace y by $\psi = \psi(x,t)$ to denote that it is a function of x and t, and we replace u by $\nu\lambda$, so that

$$\frac{\partial^2\psi}{\partial x^2} = \frac{1}{\nu^2\lambda^2}\frac{\partial^2\psi}{\partial t^2} \tag{36}$$

where in the case of the wave motion associated with a corpuscle, we have the relations

$$E = \frac{1}{2}\mu v^2 + V(x),$$

$$\nu = E/h$$

and

$$\lambda = h/p = \frac{h}{\sqrt{2\mu(E - V)}}$$

Thus we can write (36) in the form

$$\lambda^2\frac{\partial^2\psi}{\partial x^2} = \frac{1}{\nu^2}\frac{\partial^2\psi}{\partial t^2} \tag{37}$$

Assuming a solution for $\psi(x,t)$ of the form

$$\psi(x,t) = \Phi(x)\cdot\epsilon^{2\pi i\nu t}$$

where the exponential factor may be replaced by either Cos $2\pi\nu t$ or Sin $2\pi\nu t$, we obtain from (37) the differential equation

$$\frac{\partial^2\Phi}{\partial x^2} + \frac{4\pi^2}{\lambda^2}\Phi = 0$$

that is,

$$\frac{d^2\Phi}{dx^2} + \frac{8\pi^2\mu}{h^2}(E - V)\Phi = 0 \tag{38}$$

In this case, where Φ is a function of x only, the partial differential is the same as the ordinary differential coefficient.

Equation (38) is the form of Schrödinger's P. D. E. for *one coördinate* and it will be observed that since V is a function of x, the equation cannot be solved in the same manner as (25) where the coefficient of $f(x)$ was assumed to be a constant. The exact technic of solution thus depends upon the form of the function V.

The simplest case is that of a particle moving freely, for which, therefore, $V = 0$. In analogy with equation (25) the solution is then of the form

$$\Phi = A \operatorname{Sin} a\sqrt{E}\cdot x + B \operatorname{Cos} a\sqrt{E}\cdot x$$

where $a^2 = 8\pi^2\mu/h^2$.

This has physical significance if we put

$$a\sqrt{E} = 2\pi/\lambda$$

where λ is a wave length.

Consequently

$$\frac{8\pi^2\mu}{h^2}\cdot\frac{1}{2}\mu v^2 = \frac{4\pi^2}{\lambda^2} \text{ and } \lambda = \frac{h}{\mu v},$$

which is the de Broglie relation.

There is evidently no limitation on the possible values of E, and therefore the magnitude of the energy can vary continuously from 0 to any desired positive value.

Form of Schrödinger's Equation for General Case

More generally, the motion of a corpuscle will require three coördinates and V will be a function of these coördinates. Under these conditions, the wave amplitude as a function of coördinates and time is of the form

$$\psi = \Phi . \epsilon^{2\pi i \nu t}$$

where $\nu = E/h$, and Φ is a function of the coördinates only. The Schrödinger equation then takes the form

$$\Delta\Phi + \frac{8\pi^2\mu}{h^2}(E - V)\Phi = 0 \qquad (39)$$

where $\Delta\Phi$ is the so-called Laplacian operator, the exact form of which depends upon the nature of the coördinate system. Thus for Cartesian coördinates, x, y, z

$$\Delta\Phi = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Phi \qquad (40)$$

while for the spherical coördinates, r, the radius vector, Θ, the latitude, and η, the longitude,

$$\Delta\Phi = \frac{1}{r^2 \operatorname{Sin}\Theta}\left[\frac{\partial}{\partial r}\left(r^2 \operatorname{Sin}\Theta \frac{\partial\Phi}{\partial r}\right) + \frac{\partial}{\partial\Theta}\left(\operatorname{Sin}\Theta \frac{\partial\Phi}{\partial\Theta}\right) + \frac{\partial}{\partial\eta}\left(\frac{1}{\operatorname{Sin}\Theta}\frac{\partial\Phi}{\partial\eta}\right)\right] \qquad (41)$$

If the Schrödinger equation can be solved at all it will be found possible to separate the terms into groups, each involving only one of the variables. By introducing one or more arbitrary parameters, such as $-m^2$ in the case of equation (25), the original P. D. E. is replaced in this manner by as many *ordinary differential equations* as there are variables.

Thus the solution of the Schrödinger equation for any problem reduces to the solution of an ordinary differential equation of a form which is quite familiar to mathematicians, and which is known as the Sturm-Liouville eigenvalue problem. The most general expression for this equation is

$$\frac{d}{dq}\left[f(q)\cdot\frac{dQ}{dq}\right] + [\gamma g(q) - s(q)]\,Q = 0$$

where γ is a parameter corresponding to $-m^2$ in equation (25) or to E in equation (38), and $f(q)$, $g(q)$, and $s(q)$ are functions of the coördinate q which are continuous and single-valued for the whole region to which q corresponds.

It is found that solutions of this equation corresponding to single-valued and continuous values of Q between the possible limits of q are obtainable *only for certain discrete values of the parameters* γ *or* E. These

discrete values of the parameters are known as *eigenwerte* or characteristic values (anglicized to *eigenvalues*) and correspond to the stationary energy states of the Bohr theory. Corresponding to each value of γ or E there is obtained an expression for the "amplitude" Q, as a function of q. These are known as the *eigenfunctions* or *characteristic functions* and the most general solution of the differential equation (39) will be represented as the sum of the products of the eigenfunctions for each variable obtained for the different values of the parameters γ or E.

Problem of Linear Harmonic Oscillator

As an illustration of the application of the Schrödinger method, let us consider the problem of the linear harmonic oscillator for which the relation for the total energy as deduced in a previous section is given by

$$E = \frac{p^2}{2m} + \frac{k}{2} q^2$$

The first term on the right-hand side represents the kinetic and the second term the potential energy.

As shown already, classical mechanics leads to a relation for the motion of the oscillator expressed by

$$q = q_0 \operatorname{Sin} 2\pi\nu_0 t \tag{8}$$

$$= \frac{1}{\pi\nu_0} \sqrt{\frac{E}{2m}} \cdot \operatorname{Sin} 2\pi\nu_0 t \tag{10}$$

where

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \tag{9}$$

Hence the potential energy

$$V = \frac{kq^2}{2} = 2\pi^2 m\nu_0^2 q^2 \tag{42}$$

The introduction of the quantum condition leads to the solution for the discrete energy states

$$E = nh\nu_0 \tag{11}$$

and consequently the frequency of any line in the spectrum must be given by

$$h\nu_s = h\nu_0(n_1 - n_2)$$

Since $n_1 = n_2 \pm 1$ according to the selection rule,

$$\nu_s = \nu_0.$$

For the case of one coördinate, Schrödinger's equation is of the form already given in (38). Substituting for V from equation (42) we obtain the equation, for the linear harmonic oscillator, of the form

$$\frac{d^2\Phi}{dq^2} + \frac{8\pi^2 m}{h^2} (E - 2\pi^2 m\nu_0^2 q^2)\Phi = 0 \tag{43}$$

Solutions of this equation are required for which Φ shall remain finite, continuous, and single-valued for all values of q ranging from $-\infty$ to $+\infty$ and from the form of the equation it is shown that this is possible only for those values of E which satisfy the relation

$$E_n = (n + 1/2)h\nu_0 \tag{44}$$

where E_n denotes the energy of the oscillator in the nth state. This result, it will be observed, is quite different from that derived by classical mechanics, but is in better agreement with actual spectroscopic observations.

Corresponding to any *eigenvalue*, E_n, there exists an *eigenfunction* of equation (46) of the form

$$\Phi_n^{(x)} = \epsilon^{-x^2/2} H_n(x) \tag{45}$$

where

$$x = 2\pi q \sqrt{m\nu_0/h} \tag{46}$$

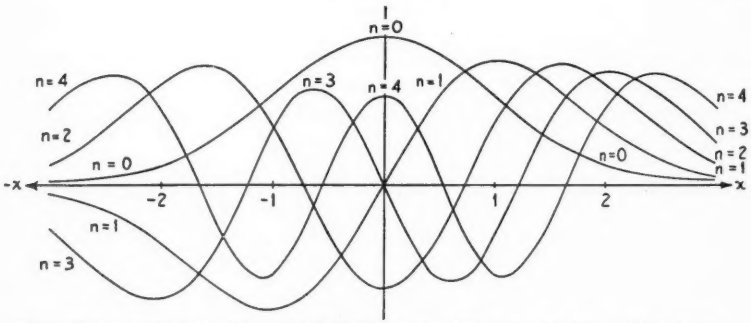


FIGURE 3.—EIGENFUNCTIONS FOR LOWER ENERGY STATES OF LINEAR OSCILLATOR
[From SCHRÖDINGER, *Naturwissenschaften*, **14**, 664 (1926).]

and $H_n(x)$ denotes a polynomial of degree n, in x, which is known as a Hermitian polynomial.

Plots of Φ_n as functions of x for $n = 0$ to $n = 4$ are shown in Figure 3 and it will be observed that the curves exhibit n points at which $\Phi = 0$ (*nodal points*) for lower values of x, while Φ decreases exponentially to zero for larger values of x.

Thus the quantum number, n, appears *quite naturally* as a result of the mathematical form of the Schrödinger equation, and corresponds to the *number of nodal points* of a vibrating string. It is no longer necessary to introduce the quantizing condition of the older quantum theory.

Properties of Eigenfunctions

In order to understand the interpretation of the function Φ, it is essential to note certain important mathematical features of the eigenfunctions which appear as solutions of Schrödinger's equations.

(1) **Orthogonality.**—The different eigenfunctions, corresponding to different values of n, form an orthogonal set, that is, in the case of functions of a single variable, x,

$$\int \Phi_n \Phi_j \, dx = 0 \text{ for } n \neq j. \tag{47}$$

where the integration is carried out over the whole region for which Φ has finite values, and Φ_n and Φ_j any two solutions.

Thus from equation (45) it may be shown that

$$\int e^{-x^2} H_n(x) \, H_k(x) dx = 0 \tag{48}$$

where n and k are different.

The simplest type of orthogonal system of functions is formed by the sine or cosine of an angle, Θ. The limits in this case are $0 \leqslant \Theta \leqslant 2\pi$, and it is readily shown that

$$\int_0^{2\pi} \text{Cos } n\Theta \text{ Cos } k\Theta \, d\Theta = 0$$

and similarly for the sine functions.

This property of the eigenfunctions is important since it enables us to develop any arbitrary function, which is continuous, single-valued, and finite for a given region, in terms of eigenfunctions in a manner similar to that used in developing functions by Fourier's methods in terms of sines or cosines.

Where Φ is a function of variables $q_1, q_2 \ldots q_f$, the integration has to be performed through the whole region of the corresponding f-dimensional space. The condition for orthogonality is then given by

$$\int \Phi_n \Phi_j \, dq_1 \, dq_2 \ldots dq_f = 0$$

(2) **Normalizing Factor.**—When the eigenfunctions are real (that is, not complex functions) it is found that a coefficient N may be derived so that

$$N^2 \int \Phi_n^2 \, dx = 1 \tag{49}$$

The factor N is said to be a *normalizing factor* of the eigenfunction and the integration is carried out over the same region as that involved in equation (47).

For the case of complex functions, Φ_n^2 must be replaced by the product of the two complex conjugate functions which are denoted by Φ_n and $\overline{\Phi}_n$. (This also holds valid for the condition for orthogonality, where $\Phi_n \overline{\Phi}_j$ should be used.)

Also, where Φ is a function of more than one variable, the integration must be performed through the whole "configurational" volume in which the system has finite values of Φ.

Thus the normalizing factor in the case of the linear oscillator is found to be

$$N = \pi^{-1/4}\, 2^{-n/2}\, (n!)^{-1/2}$$

and therefore

$$\frac{1}{2^n n! \sqrt{\pi}} \int_{-\infty}^{\infty} \Phi_n(x) \cdot \Phi_j(x)\, dx = \begin{cases} 1 & (n = j) \\ 0 & (n \neq j) \end{cases} \qquad (50)$$

Significance of Schrödinger's Function Φ

The function Φ obtained as a solution of Schrödinger's equation represents in mathematical terminology the "amplitude" of a wave motion traveling along the x-axis with velocity

$$u = \frac{E}{\sqrt{2m(E - V)}} = \frac{E}{\sqrt{2m(E - 2\pi^2 m\nu_0^2 q^2)}} \qquad (51)$$

It is therefore *imaginary* for values of $q > q_0$, and obviously cannot have any physical significance. Furthermore, while in classical theory, the oscillating corpuscle can never occur outside the region $-q_0$ to $+q_0$, no such limitation appears in Schrödinger's equation for the function Φ, which has finite (although vanishingly small) values for regions which are external to the classical limits.

Hence the eigenfunctions cannot represent amplitudes of a physical wave motion such as that associated, for instance, with acoustical vibrations. In fact, when we consider that Schrödinger's Φ may represent a function of six coördinates in the case of the two electrons in a helium atom, it is evident that such a naïve interpretation of the function is inconceivable.

It will be remembered that when the electromagnetic wave theory was first postulated it appeared necessary also to postulate a medium, the ether, in which electromagnetic waves are transmitted. As is well known, all attempts to demonstrate the existence of such a medium, as, for instance, the famous Michelson-Morley experiment, have yielded negative results, and the reason for this was provided by the theory of relativity. Furthermore, regarding the nature of electromagnetic energy, it has been found necessary to postulate a dualistic conception, so that on the one hand we have undulatory, and on the other, corpuscular attributes. To bridge this apparent contradiction Einstein suggested that the electromagnetic field in a given region determines the relative probability that the photons go to different places. "In a set of interference fringes, the wave amplitude is strong at some places and weak at others. The quanta go to the different places with a *relative probability* that is given by the wave measure of the intensity, namely, the *square of the wave amplitude* (*8*)."*

* The writer is responsible for the italicized portions.

Following this suggestion, Born has put forward a similar interpretation of Schrödinger's function, Φ. The *intensity* of the de Broglie wave motion, that is, *the square of* Φ, represents the relative probability of a certain configuration of the system. In the case of one particle, in motion along one coördinate, q, the average probability of occurrence of the particle in the region between q and $q + dq$ is thus given by

$$Pdq = \Phi^2 dq \tag{52}$$

Similarly, if Φ is a function of three or more coördinates the probability of occurrence of the system in a region defined by the elementary "volume" $dq_1\, dq_2 \ldots dq_n = dv$ is

$$Pdv = \Phi^2 dq_1\, dq_2 \ldots dq_n. \tag{53}$$

It is this conception of Φ^2 that replaces in Schrödinger's mode of calculation the classical "orbit." As pointed out previously this interpretation follows logically from the principle of indeterminism, and, indeed, supplements it by making the whole idea more precise mathematically. Whereas classical mechanics, by postulating exactly defined initial values of coordinates and momenta, enables us to determine the future behavior of a given system in every detail, the new mechanics finds that the initial state is indeterminate and that therefore we can calculate only the manner in which a wave of probability will be refracted in the field of force due to the interaction of the various particles of the system.

Probability Calculations for Linear Harmonic Oscillator

The interpretation from this point of view of the eigenfunctions Φ_n in the case of the linear harmonic oscillator illustrates very well the significance of the point of view of the new mechanics.

It is first, however, necessary to discuss briefly the deductions regarding the probability distribution which are derived from classical considerations (*9*). In terms of the variable x, defined by equation (49), the maximum amplitude of the motion is given by

$$\begin{aligned} x_0 &= (2\pi\sqrt{m\nu_0/h})q_0 \\ &= \frac{(2\pi\sqrt{m\nu_0/h})\ \sqrt{(2n+1)h\nu_0/4m}}{\pi\nu_0} \\ &= \sqrt{2n+1} \end{aligned} \tag{54}$$

Hence P is zero for $|x| > |\sqrt{2n+1}|$, while for values of x within the limits of oscillation P must vary inversely as the velocity of the particle at any point. This leads to the conclusion

$$P = \frac{1}{\pi\sqrt{2n+1-x^2}} \tag{55}$$

That is, the probability approaches infinitely great values as x approaches its limiting values, and within this range the function P must be represented

by a curve such as that shown in *B*, Figure 4, for the different values of n. In these curves, the ordinate corresponds to the probability, and the abscissa denotes the value of x.

It will be observed from equation (55) that

$$\int_{-x_0}^{x_0} P dx = 1$$

That is, the total probability of occurrence of the particle anywhere in the region between $-x_0$ and $+x_0$ is unity.

On the basis of Schrödinger's solution, Φ_n has finite values even for values of x outside that defined by the classical limits, and is given, in accordance with Born's suggestion, by the relation

$$P dx = \frac{1}{2^n n! \sqrt{\pi}} \cdot \epsilon^{-x^2} H_n(x)^2 dx \qquad (56)$$

where the normalizing factor has been inserted in order that we may fulfil the condition

$$\int_{-\infty}^{\infty} P dx = 1$$

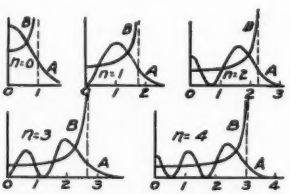


FIGURE 4.—PROBABILITY OF OCCURRENCE OF OSCILLATING PARTICLE ACCORDING TO QUANTUM MECHANICS (CURVES A) AND ACCORDING TO CLASSICAL THEORY (CURVES B)
(From Condon & Morse, "Quantum Mechanics," p. 51.)

Equation (56) thus denotes the probability of locating the oscillating particle in the region between x and $x + dx$, when it is in the nth energy state, defined by E_n.

The corresponding probability distribution curves for different energy states as derived by means of equation (56) are indicated in the curves *A* in Figure 4 and as will be observed, $\Phi_n^2 dq$ has a *finite value even for regions outside the limits of classical oscillation. In other words, there exists a finite probability that the oscillating particle will occur for a part of the time in regions which are forbidden by classical mechanics.* For the state $n = 0$, it is readily shown that there is a 15.73 per cent chance that this will occur, or in the lowest energy state, the oscillating particle occurs on the average 15.73 per cent of the time in regions outside that fixed by classical theory.

This conclusion is evidently at variance with classical dynamics, since it signifies that a particle has a measurable probability of occurrence in a *region in which the potential energy is greater than the total energy.* It is, however, just this type of deduction which has been applied by Condon and Gurney, and independently by Gamow, to account quantitatively for radioactive phenomena, while Fowler and Nordheim and also Oppenheimer have incorporated the same idea in order to account for cold cathode emission of electrons.

The Hydrogen Atom

As another illustration of the application of Schrödinger's equation, let us consider the case of the hydrogen-like atom—a system consisting of one electron and nucleus of charge Ze. *Classically* the problem of determining the energy levels and electronic orbits is solved in the following manner:

(1) Using polar coördinates (r, Θ) the kinetic energy, T, and potential energy, V, are given by

$$T = \frac{\mu}{2}(\dot{r}^2 + r^2\dot{\Theta}^2); \quad V = -\frac{Ze^2}{r} \tag{57}$$

In the Hamiltonian form, the total energy (H) is expressed in terms of the coördinates and corresponding momenta. From equation (57) it follows that

$$E = H = \frac{1}{2\mu}\left(p^2_r + \frac{p^2_\theta}{r^2}\right) - \frac{Ze^2}{r} \tag{58}$$

(2) The equation for H is transformed into the Hamilton-Jacobi partial differential equation (P. D. E.) by putting

$$p_r = \frac{\partial A}{\partial r}; \; p_\Theta = \frac{\partial A}{\partial \Theta}$$

where A is a function of r, Θ, and E which is known as the "action." The resulting P. D. E. is of the form

$$\left(\frac{\partial A}{\partial \Theta}\right)^2 - r^2\left\{2\mu E + \frac{2\mu Ze^2}{r} - \left(\frac{\partial A}{\partial r}\right)^2\right\} = 0 \tag{59}$$

This equation is then separated, by introducing an arbitrary parameter, into two ordinary differential equations, one involving r, and the other Θ.

(3) The quantum conditions are introduced in the form:

$$\left.\begin{aligned} \oint \frac{dA}{d\Theta}\, d\Theta &= kh \\ \oint \frac{dA}{dr}\, dr &= (n-k)h \end{aligned}\right\} \tag{60}$$

where n may have any integral value from 1 to n and $k = 1, 2 \ldots n$.

(4) This leads to the following results:

(*a*) Discrete energy states defined by the relation

$$E_n = \frac{-2\pi^2 Z^2 e^4 \mu}{n^2 h^2} \tag{61}$$

(*b*) Elliptic orbits for the electron for which

$$\frac{b}{a} = \frac{\text{minor axis}}{\text{major axis}} = \frac{k}{n}$$

(*c*) Frequency of revolution of electron as a function of n.*

While in the classical treatment correct results are obtained for this problem by treating it as one involving only two degrees of freedom, it was shown by Schrödinger that in the wave mechanics method neglecting any degrees of freedom is apt to lead to incorrect results. This is especially true of the hydrogen atom problem. Consequently, the Schrödinger equation for this system must be expressed in three coördinates, and the classical analogy suggests the spherical coördinates r, Θ, and η. Consequently the Schrödinger P. D. E. is of the form

$$\Delta\Phi + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r}\right)\Phi = 0 \qquad (62)$$

where the Laplacian operator, $\Delta\Phi$, is expressed by equation (41).

Differential equations of this type are obtained in many fields of physics, as for instance, problems of potential, heat diffusion, propagation of waves, etc., and the procedure for solving them is therefore well known. It is assumed that a solution of equation (62) can be found, of the form

$$\Phi = R(r) \cdot F(\Theta) \cdot G(\eta) \qquad (63)$$

where each function involves only one of the variables. The solution must be subject to the boundary conditions that Φ is finite, single-valued, and continuous for

$$0 \leq \Theta \leq \pi$$
$$0 \leq \eta \leq 2\pi$$
$$0 < r < \infty$$

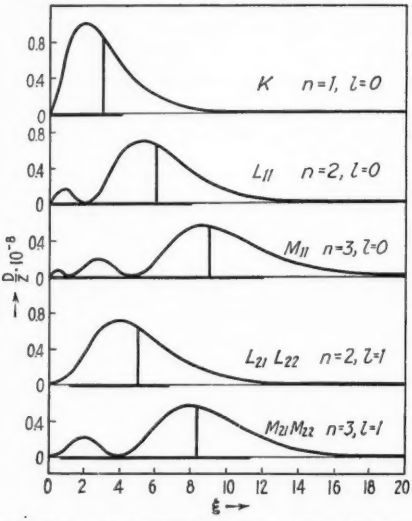


FIGURE 5.—EIGENFUNCTIONS FOR LOWER ENERGY STATES OF HYDROGEN ATOM

[From PAULING, *Proc. Roy. Soc.*, **A114,** 181 (1927); see also Ref. (*10*).]

The result of the mathematical procedure shows that solutions satisfying these conditions are obtainable only for those values of E which are given by equation (61), and which therefore are defined by a quantum number, n.

* Since E_n, as well as the frequency of revolution are independent of k, the problem solved by this procedure is that of the degenerate states. It is only when the electron is subjected to a perturbing field that E as well as the frequency of revolution becomes a function of both n and k.

Instead, however, of deriving orbits from the solution of (62), expressions are obtained for the eigenfunctions, Φ, corresponding to the different values of E_n. These functions are of the form

$$\Phi_{nlm} = R_{nl} F_{lm} G_m \tag{64}$$

where the subscripts indicate that each of these functions involve certain ones of the quantum numbers

$$\begin{aligned} n &= 1, 2, 3 \ldots \\ l &= 0, 1, 2 \ldots (n-1) \\ m &= \pm l, \pm(l-1) \ldots \pm 1, 0 \end{aligned}$$

It will be observed that these numbers are brought into the resulting expression for Φ_{nlm}, not through any quantizing conditions, but naturally, through the mathematical procedure for solving the P. D. E., just as the number of nodal points was obtained in solving the problem of a vibrating string. In both cases these "nodal" numbers occur logically because of the natural boundary conditions. Thus in the wave mechanics solutions of problems, there are as many quantum numbers (n, l, m) as there are variables, (r, Θ, η), and these numbers correspond to the number of nodes for each particular coördinate.

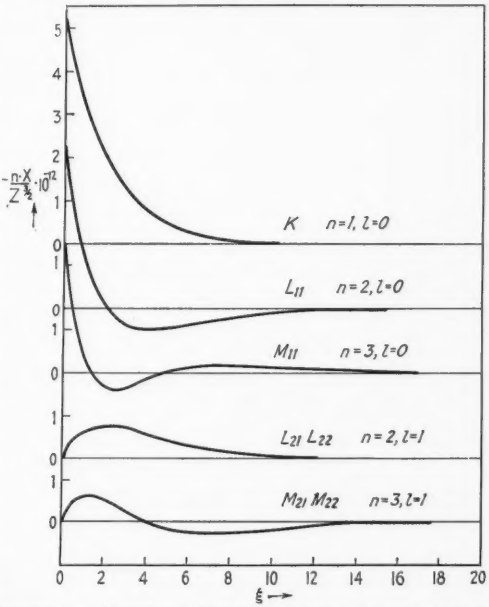


FIGURE 6.—ELECTRON DISTRIBUTION FOR LOWER ENERGY STATES OF HYDROGEN ATOM
[From PAULING, *Proc. Roy Soc.*, **A114**, 181 (1927); see also Ref. (*10*).]

The expressions for the eigenfunctions in equation (64) are in general rather complicated, but they assume a somewhat simplified form for $l = 0$, and $m = 0$. For these cases, the function F and G reduce to constants and Φ_{n00} becomes a spherically symmetrical function and therefore a function of the radius only. Figure 5 shows plots of the normalized eigenfunctions for a few of the lower energy states of a hydrogen-like atom. The abscissa is a dimensionless quantity defined by the relation

$$x = 2Zr/(na_0)$$

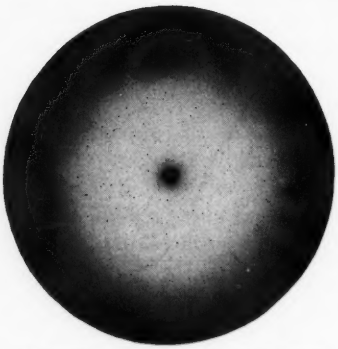


FIGURE 7.—ILLUSTRATION OF PROBABILITY OF OCCURRENCE OF ELECTRON FOR NORMAL STATE OF HYDROGEN ATOM ($n = 1, l = 0$)

where a_0 = radius of normal Bohr orbit

$$= \frac{h^2}{4\pi^2\mu e^2} = 0.528 \times 10^{-8} \text{ cm.}$$

As shown in the figure, Φ decreases exponentially (as $\epsilon^{-x/2}$) for values of r which exceed those corresponding to the classical Bohr orbits, so that Φ actually has significant values only for values of r which do not exceed greatly those derived from the Bohr theory and which are given by the expression

$$a_n = \frac{n^2h^2}{4\pi^2\mu e^2 Z} \qquad (65)$$

From the point of view, however, of the quantum mechanics, we are not interested in the form of the function Φ, but rather in that of the probability distribution function $\Phi\bar{\Phi}dv$ where dv is an element of the three-dimensional space of which the coördinates are r, Θ, and η. For spherically symmetrical eigenfunctions, we may put

$$dv = 4\pi r^2 dr$$

Thus $4\pi\Phi\bar{\Phi}r^2dr$ is to be interpreted as the probability of locating the electron in a spherical shell of thickness dr and mean radius r.

Figure 6 taken from the treatise by L. Pauling and S. Goudsmit (*10*) show the electron distributions for some of the lower energy states, plotted against values of $x = 2Zr/(na_0)$ as abscissae. The vertical lines correspond to the average values of r, and it will be observed that the positions of these lines are close to the upper limits of r as determined from classical theory.

The difference in point of view between the classical Bohr theory and the new quantum mechanics is thus seen to be fundamental. According to the older theory, the electron revolves in a definite orbit for which the maximum distance from the nucleus is indicated by the upper value of r shown in the heavy horizontal lines in Figure 6. But on the basis of the

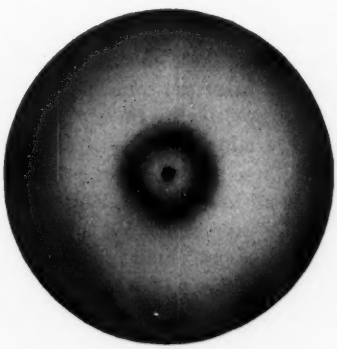


FIGURE 8.—ILLUSTRATION OF PROBABILITY OF OCCURRENCE OF ELECTRON FOR FIRST EXCITED STATE OF HYDROGEN ATOM ($n = 2, l = 0$)

new theory, the *conception of a definite orbit is replaced by that of a certain region in the space surrounding the nucleus for which the probability of occurrence of the electron is a maximum, whereas this probability decreases rapidly to zero as r is increased beyond the classical values.*

The photographs shown in Figures 7 and 8 illustrate this interpretation even more graphically.* If we could imagine the electron in a hydrogen atom replaced by an infinitesimal source of light, the net effect of the fluctuation in the instantaneous location of the electron over a period of time would result in an image which would be brightest at those points where the probability of occurrence is greatest.

Probabilities of Transitions

It will be remembered that in the Bohr theory transition probabilities were derived by application of the Correspondence Principle. This led to the deduction of selection principles by which the probabilities of certain types of transitions were forbidden, but in the case of "allowed" transitions the probabilities or intensities could be calculated only by extrapolating from conclusions deduced by the Correspondence Principle for large quantum numbers. On the other hand, the quantum mechanics of Heisenberg and Schrödinger enables us to calculate the relative intensity as well as the state of polarization of the radiation emitted as a result of any transition $n_1 \longrightarrow n_2$ from a consideration of the form of the corresponding eigenfunctions. In fact the intensity depends upon the magnitude of the product of these eigenfunctions averaged in a proper manner over the whole region in which these functions have finite values.

As D. Villars has pointed out, this eliminates the puzzling question, "What happens during an electron jump?" which worried us in the older theory. The quantum mechanics relation for transition probability may be regarded as indicating the probability that when the electron is in state n_1 and at the point x it will absorb or emit a photon and change to state n_2. The observed transition probability will thus be the average of these individual probabilities taken over all possible values of x.

From this point of view, the selection principles of the Bohr theory appear merely as statements that certain types of transitions are considerably less probable than other types, but are *not absolutely improbable.* This deduction is in agreement with actual observations on certain "forbidden" lines in nebular spectra.

* These were obtained by Mr. F. Benford by photographing the diffuse light passing through a rotating disk which had sectors cut out of such a form that the light passing through would have a radial distribution of intensity corresponding to the ordinates in Figure 6.

Aperiodic Phenomena

So far we have dealt with Schrödinger's equation expressed in terms of space coördinates only. In solving the P. D. E. (36) for a wave motion along one coördinate, there was obtained a solution $\psi(x, t)$, of the form

$$\psi(x, t) = \Phi(x) \cdot \epsilon^{2\pi i \nu t} \tag{66}$$

where $\nu = E/h$, and E is expressed on the basis of the theory of relativity as $E = mc^2$.

Differentiating this yields the relation

$$\frac{\partial \psi}{\partial t} = \frac{2\pi i E}{h} \Phi \epsilon^{2\pi i Et/h}$$

$$= \frac{2\pi i E}{h} \psi$$

Hence Schrödinger's equation

$$\Delta\psi + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$$

becomes

$$\Delta\psi - \frac{8\pi^2 m}{h^2} V\psi - \frac{4\pi m i}{h} \cdot \frac{\partial \psi}{\partial t} = 0 \tag{67}$$

in which ψ is expressed as a function of t as well as of the coördinates and E has been eliminated.

This equation is useful in dealing with aperiodic phenomena such as those involving collisions between atoms or atoms and electrons. As an illustration of an application of this equation may be cited the very interesting discussion of the problem of energy transfer between excited atoms which are in "resonance" or near-resonance, by H. Kallmann and F. London (*11*).

Energy Levels and Distribution Probabilities for Helium Atom and Hydrogen Molecule

The problems discussed so far have dealt with systems consisting of one or two corpuscles at most. However, it has been found possible by the new mechanics to treat in a similar manner more complex systems. As an illustration, we shall discuss briefly the essential features of the method used in the case of the helium-like atom consisting of two electrons and a nucleus of charge Ze.

The principal difficulty in solving this problem by classical mechanics arose from the fact that the relative phases of the two electrons could not be determined. But in the new mechanics the notion of instantaneous state, that is, definite arrangement of electrons for a given state, disappears along with the conception of electronic orbits. It is, indeed, the most striking feature of the present theory that it eliminates such considerations of individual occurrences, and surveys at one glance, as it were, all possible

configurations of the two electrons as determined by the variation in space of an eigenfunction, Φ. Actually this function is the product of the eigenfunctions of each electron and the problem consists in determining the nature of the function Φ in presence of a perturbing potential energy due to the interaction of the two electrons. The problem is reduced in this manner to the familiar mathematical problem of solving the non-homogeneous differential equation

$$\Delta\Phi + (E - V_0 - V_1)\Phi = 0 \tag{68}$$

where V_0 is the potential energy of the two electrons with respect to the nucleus and V_1 the potential energy due to their interaction. Since the solution for the corresponding homogeneous equation

$$\Delta\Phi + (E - V_0)\Phi = 0 \tag{69}$$

is known, the solution of (68) may be obtained by well-known methods.

In the case of excited states of the helium atom, the problem becomes more difficult, since each electron may be regarded as at one instant in a state n_1 and at the other in state n_2, while in the next instant they exchange places. This phenomenon has to some extent a classical analog in the observation that for two identical systems vibrating with frequency ν when separated, the frequency fluctuates between $\nu + \Delta\nu$ and $\nu - \Delta\nu$ when the systems are coupled. In this case the magnitude of $\Delta\nu$ depends upon that of the coupling force, and similarly the interaction of the two electrons in the helium atom leads to a *quantum mechanical resonance or equivalence phenomenon* and the resulting eigenfunctions and energy states may be calculated by application of the method of perturbations.

It should be observed in this connection that the electron spin introduces a factor for which no classical analog exists. However, the Pauli exclusion principle provides a guide by which a choice may be made of the proper form of solution for problems in which the question of the relative directions of spin of two or more electrons or *nuclei* must be considered. In this manner also the heat of dissociation of molecular hydrogen has been calculated, with results that are in agreement with the experimentally observed value. Furthermore, as is well known, the new theory led to the prediction of the existence of two forms of hydrogen—the ortho and para—which observation has confirmed so brilliantly.

Concluding Remarks

It would take us far beyond the scope of the present paper even to mention the achievements of the new mechanics in the five years of its development. For the chemist it seems to promise answers for the problems of valency, catalysis, and cohesion in solids. The work of London

and Heitler, Kallman and London, Langer, Villars, Rice, Pauling, and others has shown already that in this most recent product of the theoretical physicist a tool has been created which will open up new vistas in the realm of physical chemistry, and will undoubtedly lead to many new discoveries.

It may be admitted that, at first sight, the mathematical technic of quantum mechanics appears formidable, and even a dauntless spirit may well recoil with dread at the contemplation of some of the mathematical effusions which are permeating the scientific literature. However, the writer believes that the essential features of the new point of view are not so difficult to understand. The difficulties have been due largely to the method of presentation which has been adopted hitherto by most writers on this subject. They assume a knowledge of mathematical technic on the reader's part which unfortunately most physical chemists do not possess. To remedy this state of affairs must be the objective of those who have glimpsed, as it were, some vision of the promised lands which lie behind the mountains and peaks of the mathematical camouflage.

In a recent paper in the *Scientific Monthly*, Professor E. T. Bell (*12*) has spoken of the "metaphors of quantum physics" and, if we consider the mathematics of Heisenberg and Schrödinger as merely a symbolic language for the interpretation of physical phenomena, we shall find that a great deal of the apparent mystery disappears.

Summarizing the general discussion of the methods used for solving problems by quantum mechanics it will be seen that the procedure is essentially as follows:

(1) If the problem has a classical analog, the Hamiltonian expression is obtained for the total energy as a function of the generalized coördinates and corresponding momenta.

(2) This information is now expressed symbolically in a particular type of mathematical formulation. "The exact nature of the symbols used is not specified, nor is such specification necessary."

(3) Certain operations are carried out with these symbols in a perfectly abstract manner, according to definite algebraic axioms which they satisfy.

(4) The result obtained is in the form of certain numerical relations which are then interpreted physically.

This symbolic mathematics is forced on us by the dualistic aspect of observations on both photons and corpuscles, of which the uncertainty principle is a necessary consequence, and for which the non-commutative relation between p and q is a precise formulation.

In the accompanying summary (page 1111) we have attempted to exhibit in concise form the main considerations of the present review. First of all we find that the new theory is a logical consequence of the failure of classical mechanics for atomic systems and of the experiments of Compton on

the one hand, and of Davisson and Germer and G. P. Thomson on the other. The fundamental postulate of quantum mechanics is embodied in Heisenberg's *Principle of Indeterminism*, which leads to the conclusion that instead of orbits only probabilities can be calculated. The actual calculation can be carried out by transforming the basic Hamiltonian relation for the classical problem into matrix form or a partial differential equation. There exist definite connecting links between these two methods of calculation as shown in the chart and both methods lead to identical conclusions.

SUMMARY

1. Foundations of Quantum Mechanics

(1) Failure of classical mechanics for quantum effects.

(2) Corpuscular behavior of radiation, *e. g.*, Einstein's law for photoelectric effect, and Compton effect.

(3) Undulatory behavior of electrons.

2. Dualistic Behavior of Radiation and Electrons in accordance with Heisenberg's *Principle of Indeterminism*. Classical determinism must be replaced by quantum indeterminism, for atomic systems.

3. Calculation of Probabilities

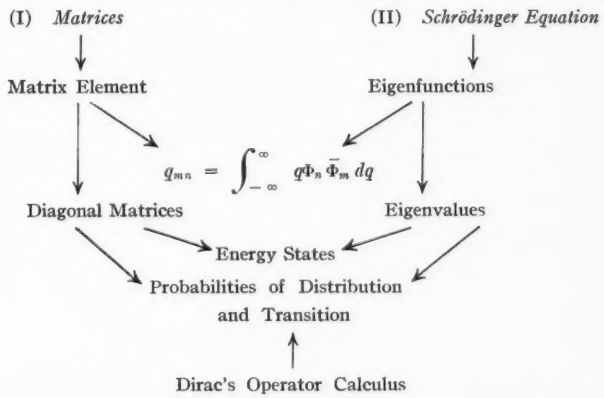
Step I. Form Hamiltonian relation for classical analog:

$$H = \frac{p^2}{2\mu} + V$$

Step II. Introduce quantum condition in form

$$pq - qp = \frac{h}{2\pi i}$$

Solve problem by either of the following methods:



As Dirac has shown, both the matrix and wave mechanics are really two special aspects of a much more general mode of treatment which may be designated the calculus of operators in an n-dimensional space. Whether this most recent development will tend to simplify the mathematical procedure remains to be seen. That it will lead, however, to some remarkable new discoveries cannot be doubted.

As perhaps a fitting conclusion to these remarks it is of interest to quote the following remarks from "The Mysterious Universe" by Sir James Jeans (*13*):

> The essential fact is simply that *all* the pictures which science now draws of nature, and which alone seem capable of according with observational fact, are *mathematical* pictures.
>
> Most scientists would agree that they are nothing more than pictures—*fictions if you like, if by fiction you mean that science is not yet in contact with ultimate reality.* Many would hold that from the broad philosophical standpoint, the outstanding achievement of twentieth-century physics is not the theory of relativity with its welding together of space and time, or the theory of quanta with its present apparent negation of the laws of causation, or the dissection of the atom with the resultant discovery that things are not what they seem; *it is the general recognition that we are not yet in contact with ultimate reality.* To speak in terms of Plato's well-known simile, we are still imprisoned in our cave, with our backs to the light, and can only watch the shadows on the wall. At present the only task immediately before science is to study these shadows, to classify them and explain them in the simplest possible way. And what we are finding, in a whole torrent of surprising new knowledge, is that the way which explains them more clearly, more fully, and more naturally than any other is the mathematical way, the explanation in terms of mathematical concepts.

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THE STRUCTURE OF ATOMS WITH PARTICULAR REFERENCE TO VALENCE*,**

HAROLD C. UREY, COLUMBIA UNIVERSITY, NEW YORK CITY

A review is given of the requirements of the Pauli Exclusion Principle and how these lead to an interpretation of the periodic system, the observed maximum valencies of elements and the promotion of electrons in the formation of molecules. The Heitler-London theory of the hydrogen molecule is very briefly reviewed to emphasize the greater need of mathematical training among chemists and references given to more extended discussions. This leads to the general theory of valence of Heitler and London and the more recent discussions of this subject by Slater and Pauling which are reviewed.

. . . . . .

In almost any discussion of the structure of atoms with particular reference to the problem of valence we shall find it profitable to review briefly the wave functions of hydrogenic atoms, that is, atoms which consist of one bare nucleus and one single electron, for a great many properties of atoms containing many electrons can be best understood in terms of these functions of the hydrogen atom. The hydrogen atom may exist in a number of so-called steady states characterized by discrete values of the energy. In order to specify these steady states it is necessary to use a number of integral or half-integral numbers which are usually taken as, first, the total quantum number, n, which in the absence of any external magnetic or electric field to a first approximation fixes the energy of the atom. The energy levels will then be given by

$$E = -\frac{Rhc}{n^2}$$

where R is the so-called Rydburg constant and is equal to

$$\frac{2\pi^2 e^4 Z^2 m}{h^3 c}$$

and n can take all integral values from one to infinity. The second quantum number which we use to discuss the steady state is the azimuthal number l which may take values ranging from 0 to $n - 1$ for any particular value of n. The l quantum number has only a small effect upon the energy values. In addition there are two other quantum numbers

* Contribution to the symposium on "Mathematics in the Service of Chemistry," held under the auspices of the Division of Physical and Inorganic Chemistry, at the 81st meeting of the A. C. S., at Indianapolis, Indiana, March 31, 1931.

** Dr. Dushman in the preceding paper has given a discussion of the quantum theory. Though his paper and this one appear under somewhat different titles they are on one and the same subject so that this paper must be regarded as a continuation of Dr. Dushman's paper and in this discussion it will be assumed that the reader has already read Dr. Dushman's general discussion of quantum mechanics and particularly of the wave equation.

we may use which are usually called m_l and m_s in case the atom is in a magnetic field, that is, if we assume that our hydrogen atoms are placed between the poles of a large electromagnet and if such is the case these two quantum numbers have a meaning. The m_l measures the angular momentum of the atom along the direction of the field, for the angular momentum along this direction is then equal to $\frac{h}{2\pi}\sqrt{m_l(m_l+1)}$ and m_s measures the component of the angular momentum along the direction of the field due to the rotation of the electron on its axis, the momentum being $\frac{h}{2\pi}\sqrt{m_s(m_s+1)}$.

Now I have described this set of quantum numbers as a convenient one. It is not the only one which can be selected. In fact, if you ask such a question as what is the shape of a single hydrogen atom, the question really has no meaning. We cannot tell what the shape of the hydrogen atom is until you tell how you are going to investigate it and then only statistically in accordance with the Indeterminance Principle. Thus, if you are going to bombard it with an electron, it will act as though it had one distribution of charge, and if you attempt to investigate it by observing the kind of light it will emit in a magnetic field, then its behavior will be described by the quantum numbers which I have given above and the distribution of charge throughout the atom can be described by using these numbers and appropriate wave functions. However, if you are going to observe the atom in an electric field the properties of the atom will again be different and so on for different conditions of investigation. Our picture of the hydrogen atom will vary, depending upon how we choose to investigate it, and, of course, exactly the same statement applies to the case of other atoms, and this is of particular importance when we wish to discuss the formation of molecules from atoms.

As Dr. Dushman has said, it is possible to discuss the hydrogen atom in terms of certain wave functions. Wave functions are in general what mathematicians call complex functions, that is, they consist of one part which is an ordinary real quantity and another part which has a factor of $\sqrt{-1}$ which we call imaginary. The wave function of the hydrogen atom or any other atom is something which we cannot measure since our measurements always deal with real quantities and not those which are multiplied by $\sqrt{-1}$. We must regard the wave function as a purely mathematical function which we will find useful in attempting to explain experimental facts. Our mathematics is a sort of machine in which we place certain experimentally observed quantities and then turn the handle and it produces for us other quantities which again can be measured. We cannot inquire too closely into any physical meaning of the intermediate steps.

A quantity which can be observed and which has physical meaning is secured from the wave function ψ by squaring it or in case it is a complex quantity by multiplying it by its conjugate. If ψ has a form $a + ib$, we multiply it by $a - ib$ and secure $a^2 + b^2$. Moreover, observable quantities which are secured in this way cannot be measured in detail, for they only give us probabilities. Thus $\psi\psi^*$ measures in the case of the hydrogen atom the probability that we shall find an electron at a certain point a certain distance from the nucleus of the atom. If we are able to observe a large number of atoms our observations would be in accord with the probable distribution for charge around the hydrogen nucleus. Nature requires us to talk about the probabilities of observing the electrons at a certain distance from the hydrogen nucleus and does not permit us to make any more definite statements about it.

We shall now review briefly the principal facts which the quantum theory requires for the distribution of charge in a hydrogen atom, that is, the distribution of a single electron about a single nucleus. The lowest energy state of the hydrogen atom is that for which the total quantum number, n, equals 1 and for which the energy equals $-Rhc$. For this state

$$\psi = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-\frac{Zr}{a}} \quad \text{and} \quad \psi\psi^* = \psi^2 = \frac{1}{\pi}\left(\frac{Z}{a}\right)^3 e^{-\frac{2Zr}{a}},$$

where Z is the atomic number, a is the radius of the first Bohr orbit,

$$\frac{h^2}{4\pi^2 Ze^2 m},$$

r is the distance from the nucleus of the point for which we wish to find the probability of finding the electron and h, e, and m are Planck's constant, the elementary unit of charge, and the mass of the electron, respectively. We see that the probability of observing an electron at a distance from the nucleus falls off exponentially from the nucleus so that there is a maximum probability that the electron is in the region of the nucleus and a very small probability that it will be at large distances. On this picture the hydrogen atom extends to infinity though the actual probability that it will be anywhere outside a small region of approximately atomic dimensions will be very small. This probability distribution is spherically symmetrical. The quantum number l has the value 0 since it cannot be greater than $n - 1$, and, of course, m_l must be equal to 0. On the other hand the m_s due to the spin of the electron may take two possible values, either $+1/2$ or $-1/2$ so that there are, in fact, two steady states of the hydrogen atom with $n = 1$, $l = 0$, $m_l = 0$, if it is placed in the magnetic field. The actual distribution of charge in either case for either state is the same. They differ only in the fact that the spin of the electron is either pointing in the direction of the magnetic field or

in the opposite direction. (Of course, we should strictly talk about the wave function associated with this spin, but it is convenient to regard it as a vector and talk about its being oriented with the magnetic field or against it, which is only an approximate way of talking about it, but sufficiently close for our present purpose.)

If the total quantum number n has the value 2, the quantum number l may take the values 0 and 1. If $l = 0$, m_l must also equal 0 while m_s may take its values $+1/2$ and $-1/2$. The charge distribution in this case consists of a centrally spherical distribution of charge of ball-like appearance, surrounded by a spherical shell where there is no charge at all, and then by a larger probability shell without a definite outer boundary, so that it decreases exponentially to zero at an infinite distance. The general character of this distribution of charge can be seen from Figure 8, p. 1106, which represents a plane through the center of the atom. The white part of the figure indicates the presence of charge while the darker parts represent regions where the charge is small so that it gives an illustration of the probable distribution of the electron within the hydrogen atom when it is in such a state. If $l = 1$ then we may have $m_l = +1$ or 0 or -1, and we have different distributions of charge depending upon whether $m_l = 0$ or ± 1. If $m_l = 0$ the probability distribution of the electron is a sort of double conical region so that most of the charge lies within the usual atomic dimensions. Figure 1 illustrates the approximate distribution of this charge. Of course it decreases to zero only at infinity, but most of the charge lies in the region as illustrated by the figure. In the case that $m_l = +1$ or -1 the distribution of charge in the atom is very nearly the same and is a sort of ring distribution as shown in Figure 2. In this case also the charge extends to infinity in all directions, but most of it lies within the region indicated by this figure. In each one of these possible choices of the quantum numbers n, l, m_l, it is possible to have a value of m_s which is equal to either $+1/2$ or $-1/2$. The distribution of charge (strictly the distribution of the probability of finding the electron at points about the nucleus) for the states with $n = 2$ are:

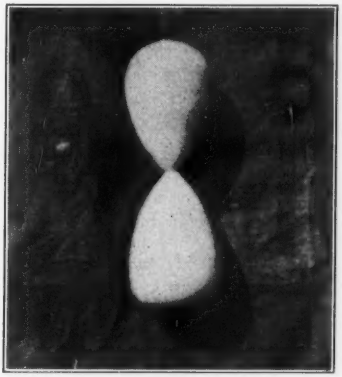


FIGURE 1.—THE CHARGE DENSITY DISTRIBUTION FOR $n = 2$, $l = 1$, $m_l = 0$

The boundaries of the figure are too sharp for the charge extends throughout space, though most of the charge lies in the region indicated by the figure.

$$\psi^2_{200} = \psi_{200}\psi^*_{200} = \frac{1}{32\pi}\left(\frac{Z}{a}\right)^3\left(2 - \frac{Zr}{a}\right)^2 e^{-\frac{Zr}{a}},$$

$$\psi^2_{210} = \psi_{210}\psi^*_{210} = \frac{1}{32\pi}\left(\frac{Z}{a}\right)^5 r^2 e^{-\frac{Zr}{a}} \cos^2\theta,$$

$$\psi_{21-1}\psi^*_{21-1} = \psi_{211}\psi^*_{211} = \frac{1}{64\pi}\left(\frac{Z}{a}\right)^5 r^2 e^{-\frac{Zr}{a}} \sin^2\theta,$$

where the subscripts of the ψ's are n, l, m_l in this order and r and θ are the radius vector and the angle between the magnetic field and the radius vector. They do not depend on the angle about the direction of the field. The first of these is illustrated by Figure 6, p. 1105, of the paper by Dushman and the latter two by Figures 1 and 2 of this paper.

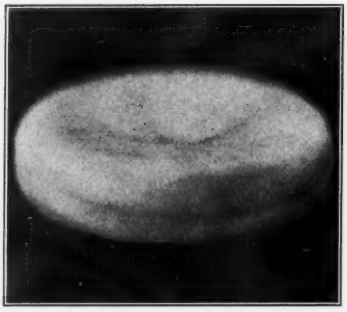


FIGURE 2A

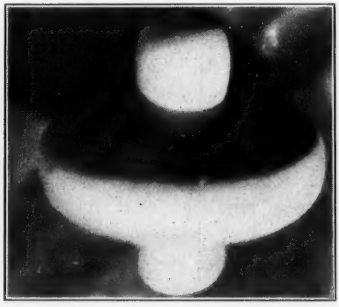


FIGURE 2B

THE CHARGE DENSITY DISTRIBUTION FOR $n = 2$, $l = 1$, $m_l = \pm 1$

See note for Figure 1. A comparison of Figures 1 and 2 gives a false impression in regard to the relative amounts of charge. The total charge of Figure 2 for either $m_l = +1$ or -1 is the same as that represented by Figure 1.

If $n = 3$ the types of distribution of charge become so involved that it is difficult to describe them briefly or to construct models illustrating them.*

So far we have been describing the various possible steady states of the hydrogen atom and possible distributions of charge within this atom on the assumption that it is in a magnetic field. We may summarize the results in the following table which lists the total number of wave functions which it is possible to have by giving the possible values of the quantum numbers n, l, m_l, and m_s. The first four rows of the table give the possible values of these quantum numbers and the last three give the number of wave functions grouped according to sub-shells and shells.

* For the general formulas for the wave functions for other states see Ref. (*1*).

TABLE I

n	1	2								3																					
l	0	0			1			0			1					2															
m_l	0	0		1	0		−1	0		1	0		−1		2		1		0		−1		−2							
m_s	±½	±½		±½	±½		±½	±½		±½	±½		±½		±½		±½		±½		±½		±½							
No. in shells and sub-shells	2	2		2	2		2	2		2	2		2		2		2		2		2		2							
	2	2					6	2					6										10							
	2				8								18																	

Thus, we see that the total number of types of steady states for the total quantum number $n = 1$, 2, and 3 are 2, 8, and 18, which can be subdivided into sub-shells dependent upon the quantum number l.

We have discussed, as I have emphasized before, the possible steady states of hydrogenic atoms and the distribution of charge of these atoms when they are in a strong magnetic field. If the hydrogen atom is in an electrical field or in the neighborhood of another atom or in a field produced by an electron or any other combination of fields, the distribution of charge within the atom will be quite different and we would choose in such cases a different set of quantum numbers and a different set of wave functions. The set of quantum numbers which we would use for such conditions will be chosen because we find it simplest to discuss the energy states in terms of them instead of those used here which are convenient for describing the atom in the magnetic field, but it is always possible to superimpose the wave function characteristic of the states of the hydrogen atom in the magnetic field in such a way that we can always get the wave function of the hydrogen atom under any set of conditions. The most recent attempts to solve the problem of valence of atoms make use of this property of wave functions. Reference to this will be made later.

It is easy to go from the principles of wave functions characterized by the quantum numbers as given in Table I to the modern explanation of the appearance of the periodic system of the elements. This is done by the well-known Pauli *Exclusion Principle* which states that any atom containing more than one electron cannot have two electrons with exactly the same wave function in the presence of a strong magnetic field. At least one of the four quantum numbers which we have used above must be different for any two electrons in the atom. If this rule is followed, we see immediately that it is necessary that the total number of electrons in the first shell, that is, electrons which have a total quantum number of 1 is 2, those which have a total quantum number of 2 is 8, those which have a total quantum number of 3 is 18, and the following numbers for $n = 4$ and 5 are 32 and 50. These are the maximum numbers of electrons with these values of the total quantum number which can be introduced in any atom. An equivalent statement of this rule of Pauli can be given

in the following way. The wave function for an atom including all its electrons and including the wave functions for the spins of the electron must always have this property: if any two of the electrons are exchanged the wave function will be the same as it was before except that the sign before the wave function will change from $+1$ to -1 or the reverse. This is commonly referred to as an anti-symmetrical wave function. This is the equivalent of the statement given above.

This rule in itself does not fix the periods of the periodic system. It is necessary to consider the question of energy as well. The question is: in any atom, which assignment of electrons to the various wave functions permitted by the Pauli principle will result in a minimum value for the energy? Spectroscopic evidence and approximate theoretical considerations in regard to this question show that the main features of the periodic system are exactly those to be expected.*

The Promotion of Electrons and Forbidden Valencies

In studying the formation of molecules from atoms some rather simple considerations will show that certain types of molecules cannot be formed. In order that two atoms shall unite and form a stable molecule, it is necessary that the energy of the system consisting of the two atoms shall decrease as they approach each other. If the potential energy decreases there will be an attraction between them and if it increases there will be repulsive forces between them. We can classify these forces acting between two atoms in the following way: (1) there is a repulsive force between the two nuclei, (2) there is a repulsive force between the electrons of one atom and those of the other, (3) there are the attractive forces between the nuclei and the electrons, and (4) there may be either an attractive or repulsive force of a character which does not occur if we think about the system in terms of our ordinary ideas in regard to positive and negative electricity and which arises from the so-called quantum resonance phenomenon. The first three of these types of forces we understood qualitatively before the invention of quantum mechanics though the exact working out of the facts will require the methods of quantum mechanics. The fourth one requires more elucidation and to do so we shall use several simple examples.

Consider, for example, the reactions written as follows:

$$\begin{aligned} H + H &\longrightarrow H_2 \longrightarrow He \\ He + H &\longrightarrow HeH \longrightarrow Li \\ H_2 + H &\longrightarrow H_3 \end{aligned}$$

Thus, the two hydrogen atoms attract each other and form a hydrogen molecule, but after the nuclei have approached to a certain distance repulsion must set in or else the atoms would telescope each other and

* See Ref. (*2*) for a discussion of this subject.

we would get a helium atom. This is due to the strong repulsion of the hydrogen nuclei. We can imagine, however, a sub-microscopic giant which could force these two nuclei together to form a helium atom. It must be a submicroscopic giant because it must be of nuclear or atomic dimensions and it must be a giant because of the energy required to force two hydrogen atoms together to form a helium nucleus. Now at the beginning of this process each of the hydrogen atoms had one electron for its lowest state, namely, $n = 1$, and we know from the Pauli Exclusion Principle that there can be but two electrons in the helium atom each one of which has a quantum number equal to 1. Thus, in this imaginary process it is possible for the electrons of the hydrogen atoms to remain in quantum states with the quantum number 1 as the hydrogen molecule passes into the helium atom. In the helium atom the electrons will be bound to the nucleus more strongly than in the hydrogen atom because of the increased nuclear charge. Thus, there will be a strong decrease in energy due to the attractive force between the electrons and positive nuclei. It is partly this attractive force which makes the hydrogen molecule possible. It is not the only consideration, however, and that will be discussed further in the following paragraphs. The second illustration we should consider is that of a helium atom and a hydrogen atom to form a helium hydride molecule and if our giant should force the helium and hydrogen atoms together we would get a lithium atom, but in the lithium atom it will be impossible now to have more than two electrons in states with $n = 1$, since at least one of these must pass to a state in which $n = 2$ and this increase in the quantum number will be accompanied by an increase in energy and this increasing energy causes a strong force of repulsion between the two. Thus, if a stable molecule HeH is to be formed it must be due to the attraction between the positive-charged nuclei and electrons causing a greater decrease in energy than this increase of energy due to the promotion of the electron so that the net energy change is negative. Without more mathematics we cannot say whether it will be positive or negative, but at least it appears very probable that HeH cannot be a stable molecule and, of course, we know from chemical data that it is not. Thus, the inert gases generally do not form compounds with hydrogen for in every case the promotion of the electron quantum numbers is necessary in order that Pauli's Exclusion Principle shall not be violated. This explains the reason for the non-existence of these molecules. In the case of the third reaction we have two electrons in the hydrogen molecule with a total quantum number $n = 1$ and we try to add to it another hydrogen atom with a total quantum number 1 and immediately it is evident that one of these electrons must pass to a higher quantum state. Thus, the molecule H_3 probably would be unstable, as is the case.

It is not always true that a promotion of the electrons in the formation of a molecule will lead to a strong repulsion between them. Thus, for example, in the formation of a molecule such as OH (this molecule exists in electrical discharge tubes and is certainly an intermediate molecule in many chemical reactions) it is necessary that the electron of hydrogen shall be promoted from a state of total quantum number, 1, to one of total quantum number, 2. Yet the OH molecule is very stable and, in fact, may be regarded as the first step in the formation of the very stable molecule water. In adding a hydrogen atom to the OH molecule, the electron must be promoted from a state of quantum number 1 to one of quantum number 2, resulting in the formation of a stable molecule H_2O, but if we attempt to add a third atom of hydrogen to water we see that the electron must enter a state with a quantum number 3 and this evidently requires such an increase in energy that the molecule H_3O is impossible. The impossibility of such molecules as NH_4, CH_5, FH_2, etc., is to be explained in the same way.

The Hydrogen Molecule

An approximate calculation for the energy of dissociation of the hydrogen molecule has been made by Heitler and London (*3*). This is a problem involving four bodies and as is well known it cannot be solved by means of straightforward mechanics. Even if the hydrogen nuclei were assumed stationary it would still be a problem of three bodies and this problem cannot be solved by simple mechanics either by using classical mechanics or quantum mechanics. It is, therefore, necessary to start with an approximate solution for the problem and then calculate correction terms.

The wave equation of the hydrogen molecule is

$$\frac{\partial^2\psi}{\partial x_1^2} + \frac{\partial^2\psi}{\partial y_1^2} + \frac{\partial^2\psi}{\partial z_1^2} + \frac{\partial^2\psi}{\partial x_2^2} + \frac{\partial^2\psi}{\partial y_2^2} + \frac{\partial^2\psi}{\partial z_2^2} + \frac{8\pi^2 m}{h^2}\left[E - \left(\frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}}\right)\right]\psi = 0,$$

where $x_1 \ldots z_2$ are the coördinates of the electrons, R is the distance between the nuclei, $r_{12}, r_{a1}, \ldots$ are the distances between electron 1, electron 2, nucleus a, and nucleus b as indicated by the subscripts. The reader can easily verify that

$$\psi_1 = \frac{Z^3}{\pi a^3} e^{-\frac{2Z}{a}(r_{a1} + r_{b2})}$$

is a solution of this equation if

$$\frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{a_2} - \frac{e^2}{r_{b1}}$$

is zero, which means that the atoms are widely separated and that electron 1 is on nucleus a and electron 2 is on nucleus b; also

$$\psi_2 = \frac{Z^3}{\pi a^3} e^{-\frac{2Z}{a}(r_{b1} + r_{a2})}$$

is a solution if

$$\frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{a_1} - \frac{e^2}{b_1}$$

is zero, meaning that the atoms are again widely separated but that electron 2 is on nucleus a and electron 1 on nucleus b. Each of these situations is equally probable and in such a situation we use two new wave functions which include some of each of these, namely,

$$\psi_S = \frac{1}{\sqrt{2 + 2S^2}} (\psi_1 + \psi_2),$$

and

$$\psi_A = \frac{1}{\sqrt{2 - 2S^2}} (\psi_1 - \psi_2).$$

The factors in front of the parentheses must be included and have values such that the following conditions hold:

$$\int \psi_S^2 \, dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \quad \text{and} \quad \int \psi_A^2 \, dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \tag{1}$$

must each be equal to 1 so that each represents the probability that the electrons will be somewhere in space, that is, unity;

$$\int \psi_S \psi_A \, dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \tag{2}$$

must be zero since this condition must hold for any two solutions of the wave equation for purely mathematical reasons. In order that these factors meet these conditions, S must equal

$$\int \psi_1 \psi_2 \, dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$$

and is a function of R. These integrals are extended over all values of the variables from $-\infty$ to $+\infty$.

The energies corresponding to the wave functions ψ_S and ψ_A are the same if the atoms are far apart, but they deviate as the atoms approach each other. These energies are

$$E_S = 2E_0 + \frac{E_1 + E_2}{1 + S} \quad \text{and} \quad E_A = 2E_0 + \frac{E_1 - E_2}{1 - S}.$$

E_1 is the mean potential energy of the system of four charged particles and is the energy contributed by their attractive and repulsive forces. E_2 is the resonance energy of quantum mechanics and it is larger than E_1. E_0 is the energy of the hydrogen atom in its normal state. The values of

$$\frac{E_1 + E_2}{1 + S}$$

and

$$\frac{E_1 - E_2}{1 - S}$$

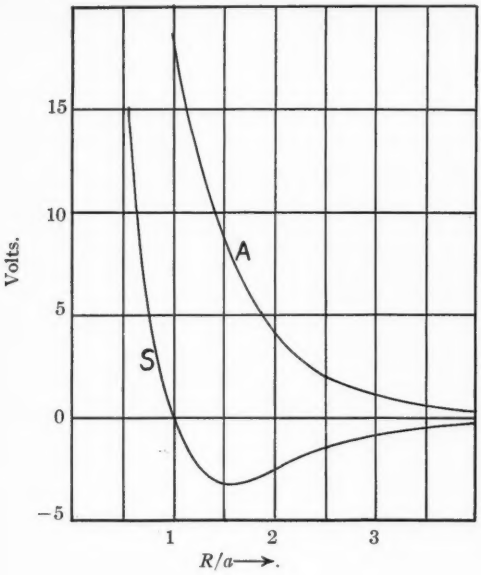


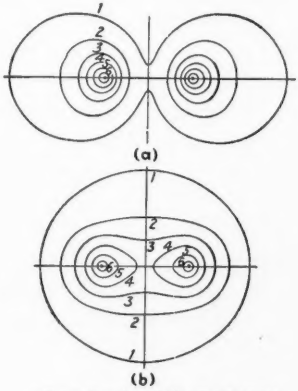
FIGURE 3

$$A = \frac{E_1 - E_2}{1 - S}, \qquad S = \frac{E_1 + E_2}{1 + S}$$

are shown in Figure 3. The former passes through a minimum showing that the atoms attract each other while the latter increases steadily as R decreases and leads to repulsion at all distances. The charge density for these two cases is shown in Figure 4 by contour lines. In the symmetric case the charge increases in the region between the two nuclei and in the anti-symmetric case in the region outside the two nuclei. Attraction occurs in the symmetric case and repulsion in the anti-symmetric case.

The wave function ψ_S does not change its sign if the electrons are interchanged (equivalent to interchanging subscripts 1 and 2) while ψ_A does change its sign if this interchange is made but does not change otherwise. ψ_S is therefore called a symmetric wave function and ψ_A an anti-symmetric one. Now the electron spins when combined give three symmetric wave functions, ψ_S(spins), and one anti-symmetric wave function, ψ_A(spins). Pauli's Equivalence Principle requires that no wave functions exist in nature which are not anti-symmetric. The entire wave function of the molecule is given by products of ψ_S, and ψ_A with ψ_S(spins) and ψ_A(spins). Thus if Pauli's principle holds the permitted wave functions are:

$$\psi_S\psi_A\,(\text{spins}) \quad \text{and} \quad \psi_A\psi_S\,(\text{spins}).$$



From Ruark and Urey's "Atoms, Molecules, and Quanta"

FIGURE 4.—THE CHARGE DENSITY OF THE HYDROGEN MOLECULE
(*a*) Anti-symmetric; (*b*) Symmetric.

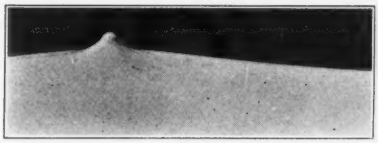


FIGURE 5.—THE ELECTRON IS ON NUCLEUS *a*

The first of these is that of the normal state of hydrogen. The ψ_A(spins) is equivalent in the vector model to the statement that the spins are oriented in opposite directions. Thus, the hydrogen molecule is diamagnetic since the angular momenta of the electron "orbits" is zero and the magnetic moment of the spins oppose each other, giving no resultant magnetic moment.

All this abstract mathematics is necessary for the solution of the problem of the hydrogen molecule, and for an exact understanding of it, it is necessary that the student be able to handle mathematics of this kind. Unless chemists in the future are going to allow physicists to do the work which has been that of chemists for a century, they will have to study advanced mathematics. It will be necessary to introduce into our undergraduate courses more mathematical subjects so that our students get a familiarity and facility in its use. Mathematics is really not difficult and is mastered by students of mathematics and physics at the same time our chemical students are learning qualitative analysis and the structural formulas of organic chemistry. Mathematicians and mathematical physicists are not exceptional people, "highbrows" as they are sometimes called. They have only had different training from the usual chemists. Such training as this must be given to our undergraduate and graduate students in chemistry in increasing amounts, and, in fact, it appears that the progress of our science is almost limited by the speed by which we can invent and learn the mathematics of the subject.

It is possible to construct mathematical models of these mathematical functions that illustrate some of the features of these molecules and the following illustrates the formation of H_2^+. Figure 5 shows a sheet stretched in a wooden frame. We can illustrate a two-dimensional hydrogen atom by thrusting a pen into this sheet to form a tent-like region. The height of the tent above the wooden frame will represent the magnitude of the wave function at a certain distance from the tent pole which is to be thought of as the position of the nucleus. The square of this quantity is a measure of the probable charge at this distance from the nucleus. A short distance from this hydrogen atom illustrated in this frame there

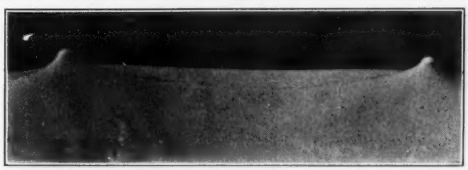


FIGURE 6.—ONE-HALF THE ELECTRON IS ON *a* AND ONE-HALF ON *b*, AND *a* AND *b* ARE FAR APART

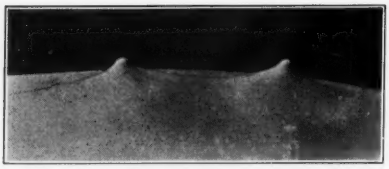


FIGURE 7.—SYMMETRIC CASE
a and *b* have approached to form the H_2^+ molecule.

may be another hydrogen nucleus (not shown). We might start out to form a hydrogen molecule by assuming that we had such a nucleus and atom, but, of course, it is equally probable that we start with the electron on the other nucleus instead of on the first. The question arises as to which we shall choose as the first approximation to our problem. The linear combination of wave functions referred to above merely means that we start with two tents, each of which is sufficiently high so that the total charge associated with each proton is just one-half an electron and then we bring these two tents toward each other. As they approach, it will be seen that the wave function builds up and becomes larger between the two nuclei (Figures 6 and 7). This represents the symmetrical method of approach of these two hydrogen atoms to each other and the charge builds up between the two nuclei as shown in Figure 4. On the other hand, it is possible to start with our two wave functions as shown in Figure 8, that is, the two wave functions are exactly out of phase so that the one extends down from the frame and the other upward. This is analogous to the situation represented by ψ_A, where the wave function is zero midway between the two nuclei and remains zero as we bring the two nuclei together. It will be seen that the wave function increases outside the nuclei and therefore that the square of the wave function increases outside of the region of the nuclei and we have a case that is exactly similar to the anti-symmetrical case of the hydrogen molecule. The first of these situations is the one which leads to attraction between the two hydrogen atoms and the additional energy can be regarded as due to the overlapping of the electron charges in the region between the nuclei while the second arrangement leads to the formation of a node between the two nuclei which means that the quantum number increases by one and we have promotion of the electron in this case. Models are always dangerous and we cannot carry them too far, but in this simple

FIGURE 8.—ANTI-SYMMETRIC CASE
a and *b* are close together.

case this represents qualitatively what is represented by the mathematics given above.

The Generalized Heitler and London Theory of Valence

Heitler and London have extended their detailed theory of the hydrogen molecules to the more general theory of valence. In hydrogen, the decrease of potential energy as R decreases occurs because the two electrons form a closed electron shell in which the two electrons have the same quantum numbers except that the spins are oppositely oriented. In the case of other atoms, it is possible to assign the valence electrons to different hydrogenic wave functions in a magnetic field so that part of these electrons are in closed shells or sub-shells ($\Sigma m_l = 0$ and $\Sigma m_s = 0$) while the rest are not and thus should be able to form closed sub-shells with electrons from other atoms, thus leading to molecule formation.

In Table I we list the possible values of the quantum numbers l and m_l for the atoms of the first part of the periodic system. These represent only the electrons of the valency shells and not those which are completely filled. To illustrate the meaning of this we may take the case of carbon. There are two valence electrons with an l quantum number equal to zero and two with $l = 1$ and $m_l = 1$ with the spins oppositely oriented. In this case no further spin coupling can occur and we would expect a valence of 0. On the other hand, if two of the electrons with $l = 1$ have different values of m_l, say $+1$ and 0, it should then be possible for the electrons from the other atoms to form pairs with oppositely oriented spins and form stable electron pairs, thus, stable electron bonds. Carbon will have a valency of two. If all four electrons are distributed with different values for l and m_l, it will be possible for the carbon atom to unite with four atoms each contributing one electron to form stable electron pairs. In this way Heitler and London attempted to explain the valencies of the elements of the first part of the periodic system and the table shows the familiar fact that the more stable valencies differ from each other by two units and that the valencies are odd for elements with odd numbers of electrons and even for atoms with even numbers of electrons. I have extended the table and included argon just to show that it is possible with the Heitler and London method to predict valencies that do not exist. The reason is that in every case it will be necessary to decide by mathematical calculations whether they really will lead to the formation of stable compounds. Obviously in the case of argon they do not. The assumption is made that an increase of the total quantum number would mean such a large increase in energy that the molecule would be unstable. In the case of argon the increase of l to a value 2 also increases the energy so much that the molecule is unstable as well.

TABLE I

Number of Electrons in the Outer Shell and Its Sub-Shells

n		$l=0$ $m_l=0$	$l=1$ $m_l=+1$	$l=1$ $m_l=0$	$l=1$ $m_l=-1$	$l=2$ $m_l=+2$	$l=2$ $m_l=+1$	$l=2$ $m_l=0$	$l=2$ $m_l=-1$	*Maximum Spin*	*Valence*
	H	1	..	..	..	..	..	..	..	$^1/_2$	1
=1	He	2	..	..	..	..	..	..	..	0	0
=2	Li	1	..	..	..	..	..	..	..	$^1/_2$	1
	Be	2	..	..	..	..	..	..	..	0	0
		1	1	..	..	..	..	..	..	$^2/_2$	2
	B	2	1	..	..	..	..	..	..	$^1/_2$	1
		1	1	1	..	..	..	..	..	$^3/_2$	3
	C	2	2	..	..	..	..	..	..	0	4
		2	1	1	..	..	..	..	..	$^2/_2$	0
		1	1	1	1	..	..	..	..	$^4/_2$	2
	N	2	2	1	..	..	..	..	..	$^1/_2$	1
		2	1	1	1	..	..	..	..	$^3/_2$	3
	O	2	2	2	..	..	..	..	..	0	0
		2	2	1	1	..	..	..	..	$^2/_2$	2
	F	2	2	2	1	..	..	..	..	$^1/_2$	1
=3	P	2	2	1	..	..	..	..	..	$^1/_2$	1
		2	1	1	1	..	..	..	..	$^3/_2$	3
		1	1	1	1	1	..	..	..	$^5/_2$	5
	S	2	2	2	..	..	..	..	..	0	0
		2	2	1	1	..	..	..	..	$^2/_2$	2
		2	1	1	1	1	..	..	..	$^4/_2$	4
		1	1	1	1	1	1	..	..	$^6/_2$	6
	Cl	2	2	2	1	..	..	..	..	$^1/_2$	1
		2	2	1	1	1	..	..	..	$^3/_2$	3
		2	1	1	1	1	1	..	..	$^5/_2$	5
		1	1	1	1	1	1	1	..	$^7/_2$	7
	A	2	2	2	2	..	..	..	..	0	0
		2	2	2	1	1	..	..	..	$^2/_2$	2
		2	2	1	1	1	1	..	..	$^4/_2$	4
		2	1	1	1	1	1	1	..	$^6/_2$	6
		1	1	1	1	1	1	1	1	$^8/_2$	8

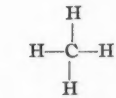
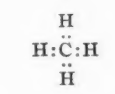
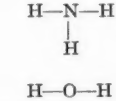
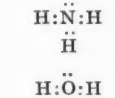
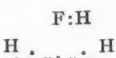
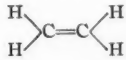
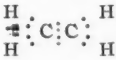
Personally I think that this scheme of valencies is not at all satisfactory, in fact, for the most part we have been presented with valencies which we as chemists do not ask for at all. Of course we talk about nitrogen being quinquevalent (you will note that it is impossible to get quinquevalent nitrogen by the Heitler and London scheme) and such things as heptavalent chlorine, but we do so because of our scheme of assigning a negative valence of two to oxygen and then counting up the number of positive valencies it is necessary to have in order to secure electrical neutrality. This is a convenient way of balancing oxidation-reduction reactions. However, in recent times we certainly have not regarded the valencies of the chlorate ion between the chlorine and oxygen atoms as polar valencies and, in fact, we do not regard the chlorine atom in this compound as being really heptavalent at all.

In Tables II and III, I have listed a number of compounds together with the usual method of writing the structural formulas by using what we may call the "classical" toothpick bond and also the formulas as written by the method of Lewis representing each of the bonds by two dots. As long as we write these formulas for the hydrogen valencies we find that the two agree fairly closely. In the case of the oxygen valencies, however, there is considerable disagreement. In the next to the last column are listed the possible assignment of valencies for these structural formulas and in the last column brief notes in regard to the shape of these molecules and groups on the basis of various evidence. Thus, the small

TABLE II

Hydrogen Valencies

All hydrogens of the simple compounds are equivalent.

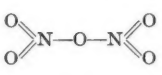
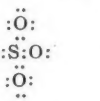
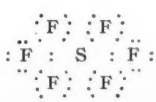
Compound	*Structural Formula* *Bond*	*Electronic*	*Valence*	*Geometrical Character*
H_2	H—H	H:H	1	Line
LiH	Li—H	Li:H	1	Line
BeH_2				
B_2H_6	?	?	3 (?)	Ethane structure
CH_4 (NH_4 +, C_2H_6, etc.)			4	Tetrahedron
NH_3 (PH_3, AsH_3, etc.)			3	Triangular pyramid
OH_2	H—O—H		2	Triangular
FH	F—H	F:H	1	Line
C_2H_4			4	The double bond supports a torque
C_2H_2	H—C≡C—H		4	Line

electric moment of CO_2 as well as the molecular spectrum data indicate that it must be nearly a straight line molecule and crystal structure data show that the carbonate and nitrate ions are plane equilateral triangles and that the sulfate ion must be a tetrahedron with the oxygens at the corners of the regular tetrahedron. The sulfur hexafluoride probably has its fluorine atoms at the corners of a regular octahedron. This table is brief but it illustrates some of the more important facts in regard to the phenomena of valence. Personally, I will not quarrel with any one as to how they wish to assign these valencies to these molecules though the method of Lewis seems to me to be preferable in many ways. It is

TABLE III

Oxygen Valencies

All oxygens are equivalent.

Compound	*Bond*	*Electronic*	*Valence*	*Geometrical Character*
CO	C═O	:C⋮O:	2 or 3	Line
CO_2	O═C═O	⋮O⋮C⋮O⋮	4	Line
$CO_3^=$ (NO_3^-)			6 or 3	Equilateral triangle in a plane
N_2O_5			5 or 3	
$SO_4^=$ ($PO_4^{\equiv}$)			8 or 4	Tetrahedron
PO_3^-			6 or 3	
SF_6			6	Octahedron

important that any theory of valence shall be able to show that these groups have approximately the geometrical structure as indicated. Thus, it appears quite evident that the simple rules of Heitler and London do not satisfactorily account for these observed facts. They are not sufficiently detailed and they postulate valencies which do not seem to exist on the basis of what appears to me to be the most rational discussion of valencies. We might point out that another question which we should like to have answered is why the characteristic double bond of organic chemistry is able to support a torque so that we have stereoisomers formed whenever such a bond exists, but we do not find them if we have only single bonds.

The Methods of Pauling and Slater* (*4*)

Slater and Pauling have shown that it is possible to construct wave functions for atoms with many electrons by taking linear combinations of

* Between the time that this paper was presented at Indianapolis, March 31, 1931, and the time of publication, a paper by Pauling (*4*) appeared presenting a very great extension of the previous work and answering several of the questions raised. It is a paper which any one interested in this subject will find of great interest.

the hydrogen wave functions discussed in the first part of this paper, which have properties suggesting directed chemical bonds of the kind long postulated by chemists. A few illustrations of these will be given.

Consider first the carbon atom which may have either two electrons with $l = 0$, and two electrons with $l = 1$ or one electron with $l = 0$ and three with $l = 1$ (see Table II). These two arrangements are usually indicated by the symbols $2s^2\ 2p^2$ and $2s\ 2p^3$, respectively. If the latter configuration is assumed it is possible to construct wave functions by linear combinations of hydrogen wave functions so that the atom has a tetrahedral symmetry with high densities of charge extending toward the corners of a tetrahedron. Four hydrogen atoms each presenting an electron to each one of these corners of a tetrahedron may couple in such a way that the s's are oppositely oriented fulfilling the requirements of the Pauli principle. At the same time a large overlapping of charge will result, giving a high energy of combination, just as in the symmetric case for the hydrogen molecule. The charge density is the same at each corner so the four bonds of carbon are exactly equivalent and methane an exact tetrahedron, just as long believed by chemists. Moreover two carbon atoms may couple in such a way that two regions of high charge density of the one atom will overlap two similar regions of another, forming a double bond. If these two atoms are rotated relative to the line joining them, the overlapping will be decreased, the energy increased and in this way a restoring torque will be introduced in exact accord the chemical facts in regard to the formation of stereoisomers.

In the case of nitrogen, the three electrons with $l = 1$ can be used to give high concentrations of electrical charge in three directions at right angles to each other and in this way we expect that the ammonia molecule will have its three bonds at right angles to each other.

Pauling has also shown that the triangular symmetry of the $CO_3^=$ and NO_3^- ions can be accounted for in a similar way and that electrons with total quantum number equal to 3 and $l = 2$ combined with electrons having $l = 1$ and 2 can give high electron densities toward the directions of the corners of a regular octahedron so that the form of SF_6 is accounted for and moreover since no electrons with $l = 2$ can be postulated for elements of the first period no such compounds as OF_6, $CF_6^=$, can be expected while SF_6 and $SiF_6^=$ are well-known molecules. This theory is in accord, of course, with the Pauli Exclusion Principle and also with the London-Heitler theory. It goes much farther than this theory, however. In particular the electron pair bond of G. N. Lewis is substantiated in nearly all its details (*5*).

Literature Cited

(*1*) DUSHMAN'S chapter in TAYLOR'S "Treatise of Physical Chemistry," Vol. 2, D. Van Nostrand Co., Inc., New York City, **1930**, p. 1339.

(2) RUARK AND UREY, "Atoms, Molecules, and Quanta," McGraw-Hill Book Co., Inc., New York City, **1930,** Chap. IX.

(3) *Z. Physik*, **44,** 455 (1927); SUGIURA, *ibid.*, **45,** 484 (1927). For a review see PAULING, *Chem. Reviews*, **5,** 173 (1928).

(4) SLATER, *Phys. Review*, **37,** 481 (1931); PAULING, *J. Am. Chem. Soc.*, **53,** 1367 (1931).

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CHEMICAL APPLICATIONS OF RAMAN SPECTRA*

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In the Raman or scattered-light spectra of chemical substances the differences between the frequency of the incident light and the frequencies found in the scattered light correspond in general to mechanical frequencies with which the atoms are vibrating in the molecule. The Raman spectra are therefore very characteristic of the molecular structure and are useful for qualitative identification, especially for isomers with structural differences. It is also possible in many cases to identify the individual Raman lines with the different types of motion of the molecule or special parts of it such as double bonds and substituent groups. This enables one to calculate the elastic strength of the chemical bonds and the thermal energy of the molecule, and makes possible the construction of a moving mechanical model of the molecule which reproduces on a large scale the motion of the atoms. Interpreting the Raman spectra in this manner one is able to calculate specific heats and entropies, and, using the energy of formation, free energies and equilibrium constants.

. . . . . .

Although modern physics has provided the chemist with a wealth of new information about the atoms and molecules with which he works, there is one outstanding deficiency in the theories of atomic and molecular structure which have been developed up to the present time, that is, their inability to deal with the molecules which contain more than two or three atoms. While it is undoubtedly of fundamental importance to understand thoroughly the simplest types of molecules, the chemist is most anxious to get some help with the problems which involve more complex molecules because it is there that he can bring to bear most effectively the vast quantity of chemical information which has been accumulated through the researches of the past one hundred years.

With this in mind it is easy to understand the enthusiasm with which the discovery of the Raman spectra was hailed. Even in the first announcements of this phenomenon it was evident that here we had a new type of spectrum, closely associated with the structure of the molecule as the chemist knows it and yielding clear-cut information even in the case of very complex molecules. Since the first paper (*1*) of Sir Chandrasekhara Raman, nearly five hundred communications have been published on the subject. It is consequently well-nigh impossible to discuss more than the outstanding features of the Raman spectra in a brief article. We shall therefore try to explain the nature and important facts regarding this type of spectrum by taking one compound as an example, namely ethyl alcohol, and showing the kind of information which can be secured that will be of particular interest for chemical research.

* Contribution to the symposium on "Mathematics in the Service of Chemistry," held under the auspices of the Division of Physical and Inorganic Chemistry, at the 81st meeting of the A. C. S., at Indianapolis, Indiana, March 31, 1931.

Experimental Technic

The experimental technic for obtaining a Raman spectrum is very simple. The most satisfactory method for general application is that developed by R. W. Wood (*2*) for liquids. It is illustrated diagrammatically in Figure 1. A mercury arc is used in order to illuminate the substance with light in which not more than two or three wave lengths are present. The light from this source (*A*) is passed through a cylindrical glass tube containing a solution which acts as a light filter in order to remove as far as possible any wave lengths of light other than those desired. This light then falls on the liquid to be studied which is contained in a glass tube about five or six centimeters long and a centimeter and a half in diameter. This tube is optically plane at one end and drawn off in a curve at the other end to avoid reflection of light.

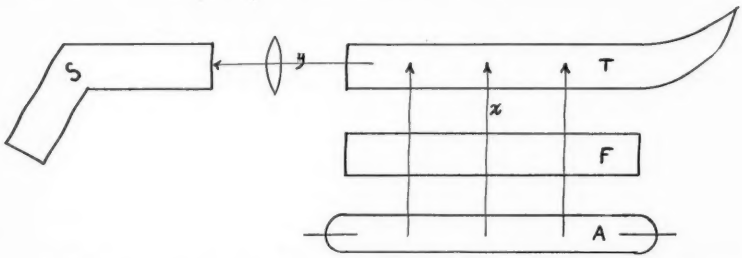

FIGURE 1.—DIAGRAM OF APPARATUS FOR OBTAINING THE RAMAN SPECTRUM

Light (*x*) passes from mercury arc (*A*) through light filter (*F*) to substance under observation in tube (*T*). There it is absorbed and scattered, and the part (*y*) coming out at a right angle to the original beam (*x*) is focused on a spectrograph (*S*).

Of the light which passes through the liquid, part is absorbed by the molecules and re-emitted as scattered light. If we focus this scattered light which comes out of the end of the tube on a slit of the spectrograph and observe its frequencies by means of a photographic plate, we find that in addition to the one or two wave lengths originally present in the light from the arc there are also a number of other new wave lengths. This is illustrated in Figure 2 which shows the sort of plate we would get if we took a photograph of the scattered light from ethyl alcohol illuminated by a mercury arc (*3*).

Nature of Raman Photographs

We presume in this case that we have filtered out all the light except that from the two lines in the mercury arc which have wave lengths 4046 A. U., and 4358 A. U., or in terms of frequency, the reciprocal of the wave length, 24,715 cm.$^{-1}$ and 22,946 cm.$^{-1}$. In our photograph we find these two

lines coming through with the greatest intensity as shown in the diagram. We also find a number of other lines of varying faintness. If the photograph is observed carefully one finds that these lines can be divided into two similar groups, one group coming from 4046 A. U., and the other from 4358 A. U. The arrows in the diagram show how the different Raman lines have originated from these two lines. The shift of the Raman line from the exciting line is indicated by the number on the arrow. It is simple to see that the shifts for the two sets of lines are the same. Experiments with the other sorts of exciting light show that the values of the shift are independent of the sources of excitation and depend only on the nature

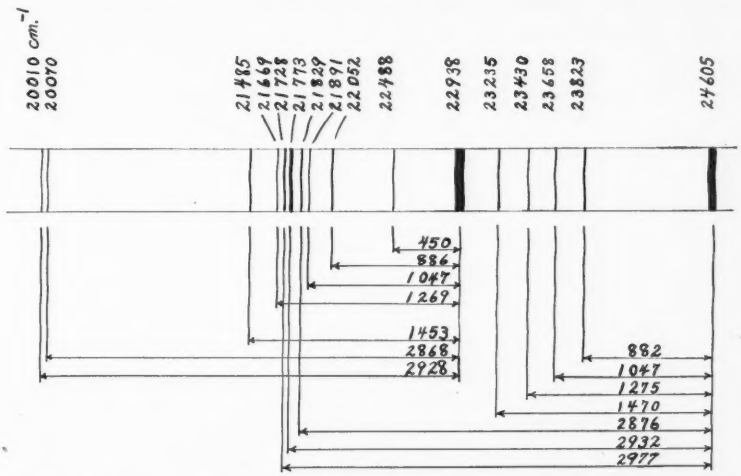

FIGURE 2.—SHOWING HOW THE RAMAN LINES OF ETHYL ALCOHOL ORIGINATE FROM THE TWO LINES (22,938 AND 24,605) OF THE MERCURY ARC

The shifts in frequency are indicated by the arrows and are practically independent of the wave length of the line of origin as may be seen by comparing to two groups. [From GANESAN AND VENKATESWARAN, Ref. (*3*).]

of the molecule which is doing the scattering. So it is evident that we have here a very powerful tool for investigating molecular structure.

To what process, then, are these shifts due? If we compare the numbers associated with the shifts to the numbers in the scale of frequencies which physics has associated with light or other electro-magnetic vibrations we find that the numbers for the shifts are the same as the frequencies in the infra-red (*4*) which have been shown to correspond to the frequencies of the vibrating motion of the different atoms in the molecule. It therefore looks as if we should investigate the nature of the motion of the atoms in the molecule in order to understand the Raman spectra.

Molecular Vibration

It has been recognized for a great many years that the atoms in the molecule are in constant motion due to the heat present in the molecule. Since we know that the same atoms always stay associated together in a particular molecule, it is evident that their motions must be vibratory in nature, for they move about some mean position while they retain essentially the same form of structure. We would expect therefore that the forces which are holding them together would be elastic in character so as to permit this vibration. It also appears that in a homo-polar molecule such as ethyl alcohol (*5*) these forces are due almost entirely to the chemical bonds and that they operate along lines connecting the atoms which have hitherto been associated with the chemical bond in a vague sort of way. It has been possible in the simplest cases to find the actual values of these elastic forces and to calculate the way they vary as the molecule is pulled to pieces. A diatomic molecule, like hydrogen for example, behaves very much like two balls joined together by a spiral spring, and in a more complex molecule we can arrive at a fair mechanical picture (*6*) of the forces and masses present by imagining the nuclei as small balls containing the appropriate masses and the chemical bonds as spiral springs which join these together.

Now although the quantum theory shows that we cannot treat the energy present in the molecule by means of classical mechanics, it is still true that the masses and forces behave in a manner almost exactly similar to the forces and masses with which we deal in large-scale mechanics. We can, therefore, tell quite easily the types of motion to be expected in a mechanical system such as that found in the molecule (*7*). For example, in a diatomic molecule the two masses will vibrate toward and away from each other with a constant frequency. This frequency (ν) will depend only on the force (k) binding the two atoms together and the masses (m_1 and m_2) of the two atoms, and the relation can be expressed in a very simple way as follows:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2} \tag{1}$$

In a more complex molecule such as ethyl alcohol it will still be possible to calculate (*8*) the frequencies if we know the masses and the strength of the forces which are tying them together, although the problem is, of course, more complicated. It has been known for some time (*6*) that the elastic strength is very nearly the same for all the bonds with which we are dealing here. Since the hydrogens are so light, this means that they will vibrate very much faster than the carbon and oxygen atoms so that we can treat their types of motion as being independent of the motion of the heavier atoms and vice versa. We would, therefore, expect the hydro-

gen to have two types of frequency, one very fast in which the hydrogen atom moves directly out along the line of the bond, and the other quite a bit slower in which the hydrogen moves perpendicular to the direction of the bond and bends it without stretching it.

As may be seen in the diagrams of Raman spectra which are included later in this article, there appear to be two groups of frequencies always associated with hydrogen, one at about 3000 cm.$^{-1}$ and the other at 1200 to 1500 cm.$^{-1}$. These are always found when hydrogen is present in the compound and are always absent when there is no hydrogen. It is apparent that these two groups are present in the ethyl alcohol spectrum. Besides this we have three lines of lower frequency.

It has been shown from a study of the classical mechanics (*8*) for such a mechanical system that we would expect the three heavy atoms to have three types of motion. These are illustrated in Figure 3. The elastic constants which have been found for the chemical bond would lead us to expect two of these to occur at about 1000 cm.$^{-1}$ and the other at about 450 cm.$^{-1}$. This is exactly what is found in the case of ethyl alcohol, so that our concept of the molecule as a system of masses (the nuclei) and forces (the chemical bonds) accounts very satisfactorily for the observed Raman spectra, if we assume that the values of the frequency shifts in the spectra correspond to the frequencies of motion of the atoms in the molecule.

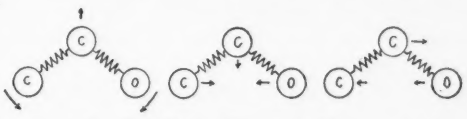

FIGURE 3.—THE THREE TYPES OF MOTION OF THE CARBON AND OXYGEN ATOMS IN ETHYL ALCOHOL
The hydrogens are not shown.

Such a simple and direct explanation seemed almost too good to be true in the early days of Raman spectra and the first theoretical treatments pointed to a more complicated explanation. As observations accumulated, however, the evidence in favor of this simple correspondence appeared quite convincing (*7*) and Van Vleck (*9*) has recently shown that it is in accord with the quantum theory for the process. There may be some few exceptions to the rule but in general we may expect a one-to-one correspondence between the Raman shifts and the frequencies of mechanical vibration in the molecule.

The nature of the Raman scattering can thus be stated very simply. According to the fundamental postulate of the quantum theory the energy in a beam of light is present in small units, the quanta. The energy of any one quantum E_i will be related to the frequency of vibration (ν_i) of the light by the equation

$$E_i = h\nu_i \qquad (2)$$

where h is the universal constant known as Planck's constant.

Now it is also true that the energy present in the *molecular* vibrations must also exist in units where the energy of a unit (E_m) is related to the frequency of vibration of the molecule (ν_m) by

$$E_m = h\nu_m \tag{3}$$

The theory which we have just postulated states that in nearly all cases a quantum of light will be absorbed by the molecule and then re-emitted, leaving behind just enough energy to give the molecule one unit of vibrational energy. Since the law of conservation of energy must hold we will have for the process

$$E_i - E_r = E_m \tag{4}$$

where E_r is the energy left in the quantum re-emitted with frequency ν_r.

Combining with equations (2) and (3) we shall have then the relation that the shift in frequency $\nu_i - \nu_r$ must be equal to the frequency with which the molecule is vibrating ν_m, *i. e.*,

$$\nu_i - \nu_r = \nu_m \tag{5}$$

Sometimes if the quantum is absorbed by a molecule which already has a quantum of vibrational energy, the light is re-emitted with its energy increased by the amount E_m. This gives rise to the so-called anti-Stokes lines where the frequency is increased instead of decreased.

A Mechanical Model of the Molecule

Since the mechanical system which has been postulated obeys macroscopic mechanical laws, it seemed worthwhile to try to construct a macroscopic model actually using spiral springs for the chemical bonds and balls of appropriate weight for the nuclei of the atoms. Such a model might show, for example, the frequencies which depended on the action of a number of atoms at once and which are very difficult to calculate from a purely mathematical consideration of the system. Such a model was constructed by Kettering, Shutts, and Andrews (*10*) as follows. With the help of the frequencies observed in the simple diatomic and triatomic molecules, it was possible to calculate quite exactly the bending and stretching constants for the average chemical bond. A spiral spring was then constructed which had the same ratio for the bending and stretching constants as the bond. Using these springs, models were made of a number of molecules and it was found that they exhibited elastic spectra very similar to the Raman spectra. A photograph of the model of ethyl alcohol is shown in Figure 4.

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FIGURE 4.—PHOTOGRAPH OF THE DYNAMICAL MODEL OF ETHYL ALCOHOL

The method of study was as follows. The model was suspended from rather weak elastic bands, and a somewhat stronger elastic band was

attached to the model at some point and pulled by a reciprocating arm driven by a variable speed electric motor. Only those impulses at frequencies which were in tune with the natural periods of vibration of the model would cause any action. When the model was agitated at one of these frequencies, however, it would go through the type of motion corresponding to that frequency. It could be observed by means of a stroboscope so arranged that the apparent motion was slow enough to be followed visually. Thus, for ethyl alcohol the analysis which had been made on the basis of the spectra was confirmed. Three types of motion corresponding to the three lowest lines in the Raman spectra were found. In these motions the two carbons and the oxygen behaved as is shown in Figure 3. The two groups of frequencies were also found for the hydro-

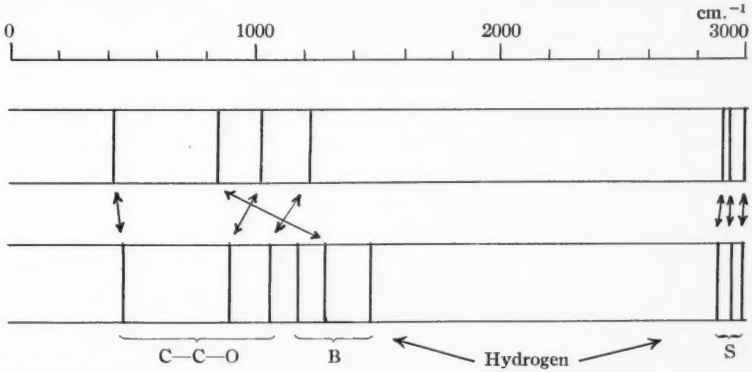

FIGURE 5.—COMPARISON OF THE FREQUENCIES OBSERVED IN THE MODEL (*upper*) AND IN THE RAMAN (*lower*) SPECTRUM OF ETHYL ALCOHOL

The frequencies of the model observed in r. p. m. have been converted to wave numbers for comparison with the spectrum by multiplying with appropriate constants.

gen as may be seen in Figure 5, the lines marked *B* corresponding to the bending of the bond and those marked *S* to the stretching.

It was even possible to distinguish the atoms principally affected by the three frequencies corresponding to the stretching of the C—H bond. The frequency at 2876 cm.$^{-1}$ caused the three hydrogens of the CH_3 group to vibrate while the others remained quiet. The frequency at 2932 cm.$^{-1}$ made the CH_2 vibrate and at 2977 cm.$^{-1}$ the O—H. The behavior of the model thus confirms the picture of the molecule which has been drawn from Raman spectra.

Determination of Molecular Structure

It is thus seen that the Raman spectra add one more step to the evolution of the chemical formula which has been taking place in the last one

hundred years. We have gone from the old idea of a molecule as representing a sort of vague association of atoms in integral numerical ratios, through the first organic formula which recognized the importance of placing bonds in definite relations to the atoms, through the extension of this formula into three-dimensional space, through the confirmation of the space picture by means of X-rays, to a dynamic picture of the molecule in which we can tell the way the parts of the molecule move and the strength of the forces which are directing these movements.

The usefulness of this to chemistry will indeed be apparent in many

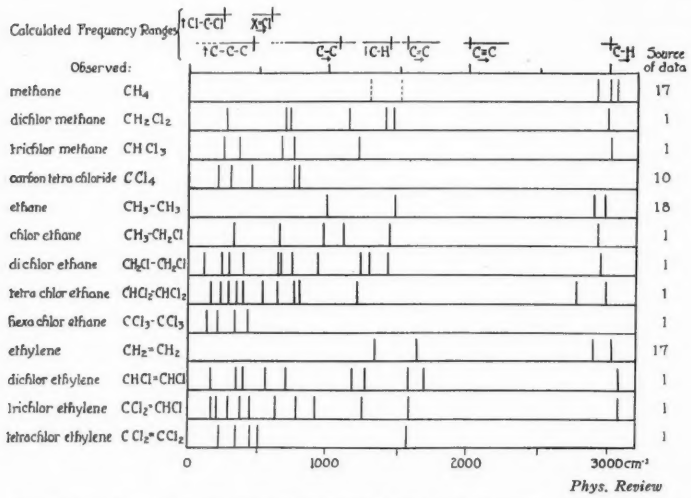

FIGURE 6.—RAMAN FREQUENCIES OF SOME METHANE, ETHANE, AND ETHYLENE DERIVATIVES

Sources of data: DADIEU AND KOHLRAUSCH, *Physik. Z.*, **30,** 384 (1929); *Ber.*, **63,** II, 251 (1930); *Wiener Ber.*, IIa, **138,** 41, 336, 420, 607, 635, 799 (1929); **139,** 77 (1930). (10) See Ref. (*3*). (17) See Ref. (*14*), second paper. (18) DAURE, *Compt. rend.*, **188,** 1492 (1929).

ways. In the first place it is extremely valuable for qualitative analysis to have an easily obtained spectrum which is so characteristic for each type of molecular structure. Again in solving the puzzle of the structure (*7*) of an unknown compound it is extremely valuable to have a means of determining the presence of such things as double bonds (*11*), secondary and tertiary hydrogen, ring structure, length of chains, and other similar points. The charts of Raman spectra in Figures 6, 7, and 8 show to some extent how this may be done. Table I gives some of the values which have been calculated from Raman spectra for the strength of the bonds.

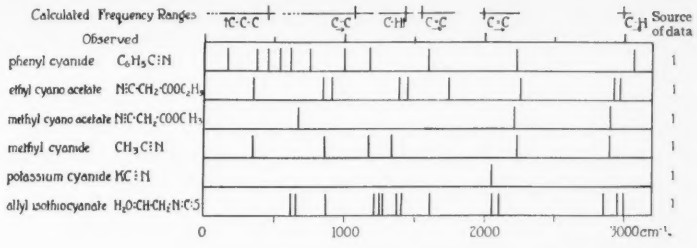

FIGURE 7.—RAMAN FREQUENCIES OF SOME COMPOUNDS CONTAINING DOUBLE AND TRIPLE BONDS

TABLE I

The Force Required to Stretch the Chemical Bond by One Ängstrom Unit

C—H	4.7×10^{-3} dynes
C—O	4.9
C—C	4.2
C=C	10.2
C≡C	14.1

Application to Inorganic Chemistry

Although in explaining the nature of Raman spectra we have discussed organic compounds only, the range of the phenomenon includes practi-

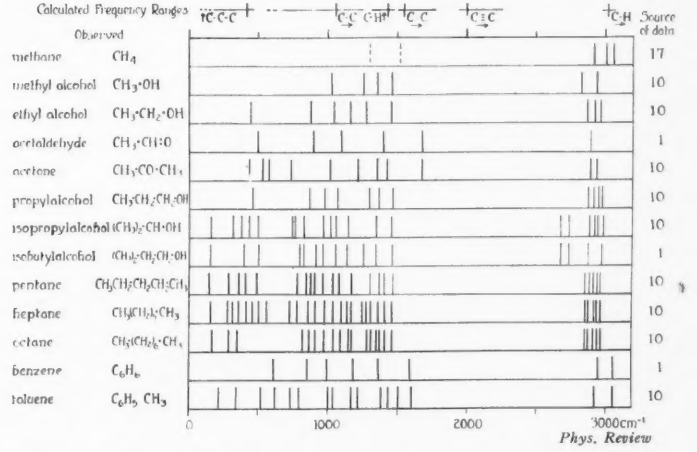

FIGURE 8.—RAMAN FREQUENCIES ILLUSTRATING THE VARIATION WITH COMPLEXITY OF THE MOLECULE

The lines above the diagram show in what region the frequencies associated with different types of bonds may be found.

cally every state and kind of matter. It has been observed in crystals (*12*), liquids, solutions (*13*) and gases (*14*) for both organic and inorganic compounds. The chief limitation seems to be that only those motions which take place under the influence of homo-polar bonds appear to give Raman lines. Thus, for example in KCN solution (*15*) we get a strong line for the vibration of the C and N against the force of the triple bond but no line for the vibration of the K, while in CH_3CN we find lines for the vibrations of all the atoms.

The Raman spectra appear to be largely independent of the nature of the environment and in solution the lines for all substances present including the solvent appear just as they would in the pure compounds (*16*). Some research has been done to see how lines might be affected by dissociation, and there is evidence that there is an effect (*17*). When more work has been done we may expect valuable information in these fields.

Calculation of Specific Heats

One of the most important chemical applications is in the calculation of specific heats (*18*). It has been shown that as a good approximation we can treat each type of motion in a molecule as behaving like a so-called ideal harmonic oscillator. By using the expression of Einstein for the specific heat of such an oscillator in terms of its frequency and temperature we can calculate (*6*) the amount of heat which any particular type of motion would absorb merely by knowing its frequency and number of degrees of freedom. Since, from the analysis of the Raman spectrum, particularly with the help of the model, we can identify the lines with the various types of molecular motion it is possible to calculate the amount of heat absorbed by each type of motion and, summing these together, to get a value which we can compare with the observed specific heat of the molecule. By integrating the specific heat we can secure values for the entropy and from this and the heat of formation, we can calculate the free energy. Knowing the free energy it is possible to estimate the equilibrium constant for any reaction of the substance with other compounds for which the free energy is known. While there is not space enough to cover the details of such calculations at this time it may be seen that we have here the possibility of investigating chemical reactions for which it might be very difficult to obtain direct experimental data.

This brief sketch may suffice to give an idea of the usefulness to chemistry of this spectrum which tells us so much about the inside of the molecule. As our picture of the nature of the molecule becomes more vivid and clear we may hope that in addition to the ordering of previously known chemical facts we shall have a stimulus toward the discovery of new realms of chemistry which otherwise might never have been dreamed of.

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AN EXPERIMENT IN EDUCATION*

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Recent discussions of the problems of higher education agree on the advisability of an active education in which the student supplies the driving force, does his own planning, thinking, and reading. Hitherto such a point of view has not been applied to any extent in the laboratory sciences. The present paper describes an experiment on this phase of the problem. Students were carried through a year's laboratory course in physiology with no formal lectures, textbooks, or laboratory assignments, devising their own experiments to answer questions arising in the class discussions. The results were apparently highly satisfactory. The present paper describes in some detail the actual conduct of the course and the evidence as to results obtained in this manner.

. . . . . .

You are all, of course, familiar with various definitions of higher education. One describes it as the process of "transferring information from the notebook of the professor to that of the student." I am not being entirely facetious in recalling this epigram, because the great majority of people look upon education in terms of the facts given or acquired. The story of the young man applying for a position who claimed to have had a college education is pertinent. His prospective employer said, "Let me see your diploma," and on learning that the young man did not carry it around with him, "Then say a five-syllable word." An education in terms of facts learned may be valid in the non-scientific divisions of knowledge (I am not competent to have an opinion on that) but certainly in science this shoots wide of the mark. We are proud in science of our method and procedures, the essence of scientific method being to accept no sort of dogmatic authority. We demand experimental, rigorously collected data, a controlled and complete examination of the whole situation; and when an "authority" or teacher in any guise makes dogmatic statements, we consider him unscientific. But now, as teachers, we do set ourselves up as authorities and expect the students to accept our word. I think this is particularly dangerous in the case of popular education at present. That is, in the great wave of popularization and "surveying" which is upon us, when the facts or the ideas of current science are given to a group of laymen in a descriptive manner, we are really saying, "This is so," or "We believe this." Such a story is no more than a modern Arabian Nights. It may be helpful; it may be stimulating; but it is really worse than useless in the sense of conveying a real idea of science. It does not inculcate the essence of science at all. Even in the case of those students who are going to deal with science professionally, although they have to know a certain number of facts, to be sure, and some technics, even for them, I think, it is more important to have a clear idea of the spirit and

* A talk delivered before the Chicago Section, A. C. S., November, 1930.

method of science than to know factual material. For several reasons. The facts that I was taught in physiology are now largely "junk," and what I am at present teaching my students will be equally worthless a generation hence. And, further, those facts which one acquires do not remain long, as we all know to our sorrow. I taught qualitative analysis for four years, but now I could not separate the copper and arsenic groups without help from a text. What *is* important is to be able, with the passage of time, to keep abreast of the new facts and ideas, to know how to find them, and still more important, how to evaluate them.

You have doubtless all heard before the things that I am saying, since education is open game in these days, but before I discuss the details of one particular experiment, there is another phase of scientific education which I wish to mention—the laboratory phase. A good deal of writing and talking about the problems of modern higher education has very little to say about the laboratory and how that may be fitted into the integrated program. You remember the famous dictum of Louis Agassiz half a century ago which really called into being our modern laboratory courses. He said, "Question nature, not books." It was a grand pronouncement and modern scientific education has been built upon it; but eventually, as the second law of thermodynamics tells us, all things decay, and in its application it has been painfully prostituted. What actually does happen in most of our laboratory courses, possibly in chemistry more than any other is this: a student comes into the laboratory with careful, detailed directions as to what he should do; he is told exactly what result to expect; and he may also be told in his manual what the interpretation is, or he may be referred to the textbook for it. In addition, the laboratory hours are usually so packed with required work that even if the student should want to think or to try some little side experiment, he just does not have the time. If he has manually executed the experiments assigned, he has filled up the period and over. In practice, the student does his experiments as per directions, makes his observations, and then looks them up in his book. If the experiment came out as expected, he has confirmed the book; and what of it? And if he did not get the result the book described, then, since it cannot be the book that is wrong, he must have made a mistake. The book is always right. We are indeed teaching our students to question nature, not books—to question what she tells us. Far from encouraging the spirit of a real examination of nature and the discovery of its laws and properties, we are really inculcating the reverse attitude. We are teaching students to believe authority in the face of nature, because only too often the experiments do not work as they should.

Well, that represents the feeling that I have, and which I suppose many others have nowadays about science teaching. The question is, what are

we to do about it? There has been given at the University of Chicago for many years an undergraduate course in physiology, running through three quarters. It has always been given in orthodox fashion and is attended usually by rather small groups of miscellaneous students, chiefly but not entirely recruited from the sciences. Two years ago, when giving that course, I got permission from the powers that be to do as I "darn pleased."

The course was announced as usual and therefore a perfectly usual group registered for it. There were nineteen the first quarter: five freshmen, nine sophomores, four from the senior college, and one graduate student. They all had had some chemistry, most of them both in high school and college and including inorganic, organic, and qualitative analysis. All but one had had physics in either high school or college. All but one had had biology, and about half had taken courses which went under the name of physiology in high school. The first day we met I gave a little set of questions to orient ourselves and to see what type of preparation the students offered. This, by the way, afforded a rather striking basis for the statement I made that facts do not stick. Incidentally, among the orienting questions asked were, "Do you know how to look up scientific information in a library?" and, "Have you ever been in the Biology Library?" Only half even claimed that they knew how to look up material, and five of those who had been here long enough to have had the opportunity admitted that they had never been in the Biology Library.

As to factual material, I asked twenty-five short questions, five each in mathematics, chemistry, physics, biology, and physiology. The following typical examples will serve:

> What is the volume of a cube, the side of which is 2″?
> What temperature Fahrenheit equals 100°C.?
> What are the common names of: NaCl, HOH, HNO_3?
> To what class of animals does the frog belong? To what phylum?
> Mention a typical reflex.

The average grade of the whole class on the questions dealing with mathematics was 63; physics, 54; chemistry, 60; biology, 54. I think you will agree that they did not constitute a particularly well-trained group, nor did they have an outstanding array of facts at their command; although they had practically all had courses covering the fields in question.

I suggested at this first meeting that, if the members of the class were willing after thinking it over, we might try the following experiment. The schedule called for three lectures and two two-hour laboratory periods a week. "Instead of lectures, let us have free discussions, and the less talking I do the better. I will not assign laboratory work—you may go into the laboratory and do the things you want. Presumably as problems are discussed in class, certain ideas will emerge that can be tested experi-

mentally; and as soon as you get such an idea, you can devise an experiment and go into the laboratory to carry it out."

We agreed to have the laboratory open continuously day and night, week-ends, and week days. The only limits on the laboratory work were: that the students must plan the experiments so as to get necessary materials during the regular hours, for the convenience of the storeroom keeper; that they had to consult with the instructor before starting an experiment, to be sure they would do no damage, that the experiment was practicable, and the necessary apparatus available; and that once an experiment was begun, it must be completed, in the sense that a definite answer was obtained to the question asked—a definite, clear-cut answer with no ambiguity, with consistent results, and with all the necessary controls—in other words, a valid piece of experimentation.

There was no textbook assigned, and I refused even to tell them the names of textbooks, though they were invited to make every use of the Biology Library. During the first week the medical librarian gave them a talk and demonstration on how to use it.

There were no formal examinations of the usual type, no attendance was taken, and there were no checks on their work, except that I did ask them to hand in certain papers; one, for example, comparing functionally the parts of the body to parts of the automobile. But at the end of the quarter, each student was expected to hand in, not a laboratory notebook, but a finished article. This was to be written as for publication, giving the initial hypotheses and facts, the reasoning, the experimental procedure and checks, the results, and the bibliography, if the problem was followed up by actual reading.

We had a vigorous discussion, the class decided to try it, and we started off. (At the end of a month I insured their continued willingness to go ahead by having them take a referendum vote in my absence.) I began by raising the question, "What is physiology?" Of course, the word "life" came up and the "functions" of the "organism." Then we proceeded to analyze what we meant by life, function, etc. I asked a few questions but gave no answers and volunteered no information; the students themselves did most of the talking and developed the subject. It was very interesting to see, at first, some student who had a bit of information proudly display it to the class, and how, after others had asked for evidence, he became much more cautious about making a statement. In discussing life, some one asked, "When does an animal die?" One replied, "When the heart stops," and another, "When breathing ceases." "But an amoeba doesn't have a heart and doesn't breathe," objected one. Then somebody else raised the question of what happens to the heart if the rest of the animal dies. And so we were well under way.

Later in the quarter, as another experimental procedure, I instituted

the practice of having some one student responsible for leading the discussion each day. He was to give a fifteen-minute talk on the subject he had specially read and worked upon, and then act as Socrates for the rest of the hour. This venture was not so successful. The leader tended to talk too long, and the others became aware of the unsuspected fact that it does take a certain amount of skill to present material intelligently. However, each one gained not a little from the experience of giving such a talk.

The first day in the laboratory each student was given a frog and told, "See what you can discover." Most of them didn't discover anything. Some, however, observed the respiration and saw the heart beat. Some of them watched the capillary circulation and wondered how anesthetics acted on it, and so on. During the first week one pair discovered that the heart can beat outside the body for several hours. It had finally stopped because it had dried up. They put the heart in water and saw that it became pale and swollen and stopped beating much sooner than in air. They actually weighed it and found that it had become heavier. Then they tried putting it in salt solution (one knew something of osmotic pressure), and thus "discovered" physiological saline or Ringer's solution, one of the major discoveries in physiology.

Most of the students were perfectly helpless at the start. Here they were in a laboratory with nothing to do. They wandered around aimlessly at first, but one by one they "clicked" and then off they went. They did experiments over a wide range of complexity. One student decided to measure the speed of a traveling nerve impulse—an experiment given in an advanced medical physiology course and one which I had never seen performed properly. He worked at it for three weeks and then demonstrated it perfectly before the class. (We instituted a program of having each group demonstrate and explain its work to the rest to partly compensate for the intense but limited efforts.) One student built a rather elaborate apparatus for measuring the basal metabolism of a frog, and, as a matter of fact, he devised several new "gadgets" as he progressed. One girl particularly impressed me because I was very dubious about her at the start. She was a typical Southern beauty and didn't look promising in a laboratory course in physiology. Before the year was over, she had become interested in the question of the relation of the ovaries to the oestrus cycle and successfully performed aseptic operations on rats. In fact, she became so enthusiastic that she took home with her that summer a colony of rats and the necessary apparatus to go on with the work.

I list below the titles of some of the papers that were finally turned in, though they may not carry much meaning to a chemical audience:

Depressor Effect of Adrenaline.
Metabolism of the Brain as Studied by Blood Sugar.

All or None Law in Nerve as Shown by Narcosis.
The Coagulation of the Blood; Isolation of Fibrinogen.
The Effect of Anisotonic Solutions on the Size of Red Blood Cells.
Perception of Small Differences in Visual Sensations: the Application of the Weber-Fechner Law to Color.
A Study of Basal Metabolism in Humans.
Observations on the Production of Beri-Beri in Pigeons.
A Study of Gastric Activity in Relation to Food and Starvation in the Human.

It will be noted that a number of the students did experiments on themselves. One girl, for example, became interested in the question of stomach contractions. She regularly came to the laboratory without breakfast, swallowed a balloon, and made mechanical records of her hunger contractions.

The students were there at all hours. I always found some one in the laboratory if I came in the evening or on Sunday. They seemed to be very much interested in the work, and at least three of their reports will eventually be published, because the experiments carried out were original with them and gave results which were new and valid.

How is one to measure the success or failure of such an attempt? I recently had a discussion at the faculty club with a physicist who said that it was ridiculous to talk of a scientific study of education because one couldn't measure its results. I offer the following evidence in an attempt at an objective evaluation of the results.

The students spent a great deal of time in the laboratory and seemed very much interested in what they were doing. They turned out, in several cases, work of the first order. In class I had the great pleasure of having a statement that I made, simply an authoritative statement, retorted to by the withering response, "My experiments show that that is wrong." I noticed at the regular departmental seminar for graduate students and faculty about three weeks after the beginning of the course that over half of these undergraduate students were present, listening to something about which they could not have understood much. The laboratory assistant in the course had been quite skeptical at the start, but about the middle of the quarter he volunteered his decision that "there really is something in it." The students did a great deal of reading in the library, and several times they brought forth items of information gleaned from the French and German scientific journals.

At the end of the quarter I gave the students a rather comprehensive questionnaire covering the workings of the course, and I think that they answered quite honestly, because there were some very fair criticisms. Here are some of the questions asked:

I. *The course as a whole.*
(*b*) 1. In what respects has it succeeded?
2. In what failed?

3. What is the most valuable thing you have gotten from the course?
4. What has bothered or displeased you most?
5. What if anything have you become really interested in?

III. *What have you gotten from the course? Compare with other courses where possible.*

(*a*) Just how have you studied in this course?
(*c*) How much time have you spent on it and how divided (laboratory, texts, articles, arguments, etc.)?
(*d*) Have you learned many facts?
(*e*) Have you learned how to get at available facts?
(*f*) Have you gained any real insight into physiology as a whole?
(*g*) Has your attitude toward science and research been altered? How?
(*h*) Has your attitude toward study (laboratory, class, homework) been different? How?
(*i*) How did you react to being put on your own initiative and responsibility?
(*j*) What is your reaction to doing semi-research in the laboratory?
(*k*) How often did you find yourself thinking about the problems raised in discussion or by your work?

A few excerpts from the answers are especially interesting.

I. (*b*) 1. The course succeeded in arousing sincere interest and a desire to work, rather than the driven attitude taken toward most laboratory courses.
2. Perhaps the course has failed to be comprehensive enough for the individual student.

II. (*a*) I like the individual laboratory work. It is something of your own on which no one else has a right to trespass. You are not trying to outdo the other fellow, but you are in competition with yourself.
(*c*) Personally, I studied more for these class discussions than any lecture course I've had.
(*e*) Personally, the amount of outside reading was much more than for any previous work. In order to get anything out of the discussions, I had to know something about it.

III. (*a*) I studied physiology to the extent that I was *taking* one course and *dragging* two.
(*b*) It was, perhaps, the first course I ever bothered to be interested in outside of classroom and study hours.
(*c*) I spent on the average of three nights a week at the library. I had several texts at home but cannot say how much time I spent studying physiology there.
(*d*) I doubt if I have learned many facts outside of a sort of laboratory method and my own experiment, though I do know something about almost all the subjects discussed.
(*e*) I can find any available facts at the library.
(*h*) I have studied because I wanted to—not because I had to.
(*i*) At first I was lost—but later I was proud of being on my own individual problem.
(*k*) Perhaps the people with whom I live can best answer [if I talked about the work out of hours]. They rejoiced when the course was over.

Another:

I. (*b*) 1. I believe the course is really an introduction to the scientific method. If it has given an impetus to one-half the people, it has succeeded. The

course cannot be measured quantitatively so the ordinary rules do not hold. So I believe it is a success because it has opened the eyes of twenty people.

2. The course has failed in that it has not given a good general background. Each person is quite familiar with one subject but quite hazy on the rest of the field. They knew something but not enough in a general way.
3. The most valuable thing I learned was the necessity of getting all the problem under controls which are indisputable. You must know what you are saying, and to do such, controls are necessary.

II. (*a*) The individual laboratory work is the best thing about the whole course. A person can play with what he is interested in, not what a prescribed manual lays down for him. Thus any individuality in his possession comes into full play. He is made to figure out his own technical problems, or develop a technic for sponging help from his neighbors.

(*c*) The class discussions were great stuff if they got started right, *i. e.*, if L. had a brain-child to expound. They generally got off the subject but something was learned and the process was inductive. This leading to rather than pouring in of knowledge is great dope. It helps later.

III. (*a*) Time in study averaged one and one-half to two hours daily. Lab. additional.

(*b*) The course was the interesting part of school. Liked mechanical part especially.

(*c*) Probably about eight hours extra a week in lab. One and a half hours in seminar and from one to fifteen hours extra weekly on extra reading.

(*k*) Always trying to figure some new system for my next experiment. Generally not paying very much attention in my other two classes, introspecting on physiology.

These are very encouraging reports and many others were in the same vein. The ultimate test, however, is what happens afterward. The course was given two years ago, and last month I took occasion to find out as best I could what had happened to the students. One of them is now doing research with me, and I asked him to undertake the rather unpleasant job of informally engaging each one in discussion and obtaining his reactions, without letting him know that the information was coming back to me. Only twelve were reachable.

He asked how much physiology the student had taken since this course. Nine out of the twelve had taken the medical courses, and nine are now doing research in the department of physiology. Some are still undergraduates and are doing their work under the title, "Undergraduate Research," a course which had to be initiated to meet their demand for a chance to continue work begun at this time. Three are working for their master's degree with me now, and another is going to study in Europe for a year and then return to work for a doctor's degree.

Another question asked was, "Did this course influence your choice of subsequent work?" At least four stated that they had had no intention of taking more physiology or of doing research, but had been led into it.

In the first questionnaire, when the students were asked to evaluate the course, they stated that they liked the attitude, that they had gotten real

insight into the scientific method, and that they felt it had been very valuable to them to be put on their own initiative; but they also felt that they had not learned as many facts as they would have in the usual course. But when they were asked this time, "How does this course compare with others in physiology you have since taken?" at least six of the nine stated that they liked the course given in this experimental fashion much better than the regular courses and were surprised to find that they learned very little new factual material even in these advanced regular courses.

Another question was, "Have you kept an active interest in the particular problem you studied?" Nearly all who are doing research have continued along lines they started at that time. One typical report turned in to me follows:

> Is doing research. Has taken other courses in physiology, 251, 252, and 407.
>
> Had no intentions of going into physiology, but took beginning courses on advice of dean. Liked the work so much that he intends to stay in physiology.
>
> Up to that time he never gave a thought as to how facts were gotten in the sciences. Just took facts as a matter of course.
>
> In later courses he did not learn very much more physiology. The laboratory work was a bore. The student cannot do an experiment the first time and do it right. Learning how to interpret results a student learns more in a course given like the beginning courses rather than the later courses.
>
> He has learned to look up material and is doing it now. Did it in other courses [in other fields].

Of course I realize that there was one thing very much in favor of this course as given, that is, its novelty. Anything new is interesting, and that gave the method tried a great advantage over the ordinary course routine. But, whatever the reason, I think the subsequent history of the students justifies the claim that they got a very real stimulus from the course, and that they were encouraged to really live their subject instead of merely hearing about it; and I am quite sure they enjoyed the work as they did it. Certainly it was the most interested and interesting class I have ever taught.

Zinc Wins Place in Auto Making. More uses are being found for the metal, zinc, in automobiles, Robert M. Curts, New Jersey Zinc Company engineer, recently told the Society of Automotive Engineers in Detroit.

Rolled, cast, and extruded alloys of zinc which show good mechanical properties and resistance to corrosion are steadily replacing more fashionable and costly metals in the manufacture of automobile parts, he declared.

Hub or tank caps, and running board molding can be made of rolled zinc plated with chromium. Die-cast alloys of zinc with copper, aluminum, and other metals have been successfully used for such things as gears or windshields.

Zinc plated or galvanized iron is coming back into favor, said Mr. Curts, for it has been found that its rival, cadmium plate, is actually less resistant to corrosion.—*Science Service*

THE "INSPECTOR-PRESENT" VERSUS THE "THOUGHT-PROVOKING" RECITATION METHOD

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By deft manipulation of questions an instructor, in conducting a recitation, may create the impression of mastery on the part of the pupils; whereas questions requiring more thought in answering may, by the responses received, show off the efforts of the teacher at an apparent disadvantage. An inspector not thoroughly acquainted with the subject matter of the course and with the goals of the instructor might be misled in the value of the teaching being done.

. . . . . .

Two recent experiences set up a train of thought in the writer's mind that led to the following conclusion: there are two rather distinct methods of conducting classroom recitations in chemistry. What is said for chemistry may probably be applied to other high-school subjects as well. The two methods mentioned might be called the "inspector-present" method and the "thought-provoking" type.

One of the experiences suggested above was that of receiving a pupil in the middle of the school year from another school where, according to his report card, he was an A and B student in chemistry. He subsequently turned out to be a D and low C student. The other experience was that of visiting a chemistry classroom where the subject matter, recently finished in the writer's classes, was being taken up. The pupils in the class visited answered perfectly practically every question asked by the instructor, while the writer's own pupils the week before had had some difficulty with the material. A consideration of the cause of these differences led to the conclusion already stated; namely, two methods of teaching.

Probably the simplest way to characterize these methods is to give a typical illustration of each. A discussion of properties of acids offers ample opportunity to point out salient differences.

Teacher—"John, what is the lesson about today?"
John—"Acids."
Teacher—"Good. Now, Mary, what is an acid?"
Mary—"Something that tastes sour."
Teacher—"That is correct; all acids taste sour because of the presence of the hydrogen ion. Name some acids, Fred."
Fred—"Hydrogen chloride, sulfuric, nitric, and vinegar."
Teacher—"Yes, and you know, of course, that vinegar is acetic acid. Now, Virginia, how is sulfuric acid made?"
Virginia—"By the contact process and the lead chamber process."
Teacher—"What do they use in the contact process?"
Virginia—"Platinum."
Teacher—"Is sulfuric acid important or not?"
Virginia—"Yes."

Teacher—"Frank, what compound of sulfur will make sulfuric acid when dissolved in water?"
Frank—"Sulfur trioxide."
Teacher—"And what acid do you get when you dissolve sulfur dioxide in water?"
Frank—"Sulfurous acid."
Teacher—"Gerald, how would you make hydrochloric acid in the laboratory?"
Gerald—"By putting sulfuric acid on salt and bubbling the gas through water."
Teacher—"Good. Now tell me, Gerald, why do you use table salt or sodium chloride in that experiment?"
Gerald—"Because it is cheap."

In order to facilitate comparison let us now present the same recitation as nearly as possible as it would be handled by a teacher using the "thought-provoking" method:

Teacher—"Today we are to discuss that large and important group of compounds known as acids. Tell me what an acid is, John."
John—"An acid is a compound that contains the hydrogen ion."
Teacher—"Contains the hydrogen ion..... How about sodium bicarbonate? That contains the hydrogen atom and might furnish the hydrogen ion in solution."
John—"Yes, but it has sodium as a positive ion also."
Teacher—"You said nothing about not having other positive ions in solution. Do you think you can improve upon your former statement?"
John—"Yes, an acid is a compound—"
Teacher—"Just 'a compound'?"
John—"An acid is a chemical compound that has the hydrogen ion as its only positive ion when in water solution."
Teacher—"Much better. Now I want some one to state as many of the properties of acids as he or she can. Mary."
Mary—"Acids taste sour, turn blue litmus red, and the stronger ones attack the metals."
Teacher—"Any corrections or additions? Ted."
Ted—"The stronger acids attack the less active metals."
Teacher—"How about sodium?"
Ted—"Oh, yes, I should have said the metals above hydrogen in the electromotive series."
Teacher—"Anything more to be said about Mary's recitation?"
Louis—"It might be added that acids turn methyl orange pink and that they all taste sour because of the presence of the hydrogen ion."
Teacher—"All right. Now name some common mineral acids. Fred."
Fred—"Hydrogen chloride, sulfuric acid, and nitric acid."
Teacher—"Is hydrogen chloride an acid?"
Fred—"When you dissolve it in water it is."
Teacher—"Then what do you call hydrogen chloride in that respect?"
Fred—"An acid anhydride."
Teacher—"Good. Now, Virginia, tell me in general how sulfuric acid is made."
Virginia—"By the contact process and the lead chamber process."
Teacher—"Those, Virginia, are two very specialized methods. I want the general steps involved in making the acid, no matter what the specific process may be. Can you tell me that? Then, Mable, you tell me."

Mable—"The general steps are the oxidation of sulfur to sulfur dioxide, the further oxidation of that gas to the trioxide, and the combination of the trioxide with water to form the acid."

Teacher—"In what place in those steps do the methods differ in the two common commercial processes?"

Mable—"In the oxidation of the dioxide to the trioxide—in the contact process platinum is used as a catalytic agent to help the action along, while in the lead chamber process nitrogen compounds are made to act as carriers of oxygen."

Teacher—"Very good. Now, Gerald, tell me how you would make hydrochloric acid in the laboratory."

Gerald—"It is made by the action of sulfuric acid on sodium chloride. The hydrogen chloride formed is bubbled through water to form the acid."

Teacher—"And why did you choose sulfuric acid?"

Gerald—"Because it is cheap."

Teacher—"If nitric acid were cheaper than sulfuric acid would it do as well?"

Gerald—"No. It would boil over too easily from the retort and would contaminate the hydrochloric acid."

Teacher—"Then what property does sulfuric acid possess that makes it well suited for making hydrochloric acid?"

Gerald—"It has a high boiling point."

The above two examples are idealized; few high-school classes would respond so readily to questioning. The reasons for the names of the two contrasted recitation methods are obvious. The "inspector-present" method is not necessarily employed exclusively when inspectors are present, since some teachers seem to use that method the year round; others use it for very apparent special occasions. Keeping in mind the fact that most of the inspectors know no more and probably even less of chemistry than the students being examined, its effectiveness can be readily seen. The "inspector-present" method is one that adapts itself easily to the instructor who is but a bare page ahead of the class. It is easy to see that in many situations it works quite nicely, because the instructor certainly has an intimate appreciation of the pupil's own troubles in preparing and understanding the lessons. At the same time, however, there are numerous occasions where the teacher's lack of background and complete training in the subject being taught might get him into something of a predicament when one of those not too uncommon precocious students asks something beyond the pages of the elementary text. Furthermore, the instructor who employs the "inspector-present" method creates in the students that satisfying feeling of knowing just about all there is to be known of the subject. The instructor benefits by the kind regard the students and their parents hold for him, because nearly every one likes things and persons associated with success, even though the success be only a high grade in chemistry.

The "thought-provoking" type of recitation, on the other hand, calls for an understanding on the part of the instructor, of subject matter that goes beyond the confines of the textbook and the training of our

educational classes, which furnish an abundance of information on how to teach but comparatively little on the thing to be taught. The teacher must have a keen appreciation and understanding of the fundamentals of chemistry and of the generalities to be drawn from that understanding. To teach by this method, so much special training in a specific subject is required that few men who get that training ever go into high-school teaching, so little are their efforts appreciated. The educators seem more interested in the teaching of "attitudes" than in the teaching of facts, as if any thinking individual could form an attitude of his own without the employment of definite and well-established facts. A deep insight into the methods of science, the long hard hours of labor needed in research, an understanding of definite cause and effect relationships, and all the other factors that go to make up a successful course in science will teach the scientific attitude automatically without too great a conscious effort on the part of the instructors.

One of the drawbacks to the "thought-provoking" method of teaching is that to an inspector, whether he be a superintendent, principal, or state inspector, the teacher appears at a disadvantage because student response to questioning is not always as spontaneous as it might otherwise be, not so self-sure as in other classes, not so self-satisfying. Students who get A's and B's in classes taught by other methods are not as satisfied usually as they might be, and their parents, especially those who have power in the community, do what they can politically to make their offspring appear to be geniuses educationally. A teacher using the "thought-provoking" method does not have an easy time of it because the average parent is not nearly so interested in how much the boy or girl has increased his ability to think, but in how high a grade he or she has received.

The use of the two teaching methods already discussed seems to divide all teachers into three classes: (1) those who employ the "inspector-present" method all the time (*very safe*); (2) those who really teach most of the time, but who fall back upon the "inspector-present" method when they deem it advisable (*very tactful*); and (3) those who are so interested in the intellectual welfare of their pupils that they employ the "thought-provoking" method all of the time (*very sincere but dangerous*).

Citric Acid from Sugar. The production of alcohol from molasses is an old story, but according to a recent article in *Commerce Reports* citric acid is being produced from cane sugar by fermentation. The process is being worked by the Tirlemont factory and Italian interests have lately acquired an 80 per cent interest in this plant. Rowntree and Co. under the Fernbach patent are making citric acid in the United Kingdom, and in Germany a large plant is being erected by the Prager Montan und Industrialwerke for citric acid production from molasses.—*News Ed., Ind. Eng. Chem.*

A LECTURE-DEMONSTRATION POTENTIOMETER AND ITS APPLICATIONS TO REDUCTION POTENTIALS IN QUALITATIVE ANALYSIS

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The sooner the student of chemistry obtains a thorough knowledge of reversible electrode reactions, the more fascinating and useful he will find the subject. The underlying theory is simple and its applications, for instance, to qualitative analysis, both varied and interesting. We find that the average sophomore can obtain a clear grasp of the subject from a few lectures, if only they are profusely illustrated with suitable experiments. We here outline our presentation of the subject to such a class and describe the construction of a semi-diagrammatic potentiometer suitable for lecture demonstrations in a large room.

The potentiometer described below can be used also for lecture demonstrations in elementary physical or electrochemistry, or for student laboratory experiments.

. . . . . .

Introduction

A clear understanding of the arrangement, operation, and theory of reversible electric cells is exceedingly useful to any student of chemistry. Reduction potentials give a quantitative measure of the driving force of many chemical reactions; showing in which direction and how far they will proceed. They enable the analyst to choose a reducing agent which will precipitate one substance without affecting others which may be present. They show him the extent of the precipitation and hence the sensitivity of the test. Finally, the simple theory of concentration cells furnishes a quick and easy way to determine the solubility of "insoluble" salts.

Despite its usefulness, the quantitative study of oxidation-reduction reactions is often postponed until late in the college course. An excellent lecture by A. A. Noyes at the California Institute of Technology in 1926 convinced the senior author that an elementary treatment of the subject offers no inherent difficulties to the student. To this lecture we are indebted for a number of the experiments, and the inspiration for much of the work described below. Assuming no previous scientific training except one year of college chemistry, we devote four lectures to the subject. In our experience sophomores with a fair knowledge of the law of mass-action grasp the subject of oxidation-reduction reactions more easily than the solubility-product principle and find it more interesting.

It is of course useless to give abstract lectures without *demonstrating* the principles at the same time. It is impossible to explain the operation of an ordinary potentiometer, in which simplicity is rightly subordinated to accuracy, and to measure potentials in such a way that a class of a hundred

will be able to see what is going on. Accordingly, after considerable thought and experimentation, we evolved an apparatus which is large enough to be visible from all parts of the lecture room; simple and semi-diagrammatic in arrangement of circuits and yet sensitive to less than a centivolt in measuring e. m. f.

Apparatus

The structural details may easily be understood by referring to the accompanying photographs and figures. The frame is made from 2-cm. white pine, 1.08 m. long. The base is 33 cm. wide. The upright piece is 42 cm. high, with a 3-mm. piece of oak (*A*, Figures 1 and 2) fastened along the top to support the slide wire (*W*). This is a piece of No. 30 B. & S. gage "advance" (constantan) wire having a total resistance of about 10 ohms. It is held in place at each end by a flat copper clamp (*C*) secured with two small brass machine screws (*B*, Figure 2).

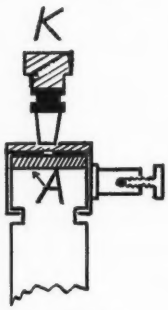


FIGURE 1
A—Oak strip
K—Tapping key

The slider (*S*) is made from a piece of sheet brass bent as shown so that the two bottom edges fit into 3-mm. square slots cut into each side of the upright 15 mm. from the top. The tapping key (*K*) is mounted on a phosphor bronze strip fastened (at *D*) to the middle of the slider and hinged so that it can be swung to either end. In this way the whole length of the slide wire can be utilized.

The metal parts are all nickel-plated, to avoid tarnishing. The wood is enameled white and the scale painted with heavy black lines spaced 1 cm. apart. Every tenth division is numbered. The connections are made with heavy, black insulated copper wire, carried as straight as possible in order that all the circuits can easily be traced. For the same reason, connection is made to the slider by means of the flexible spiral shown.

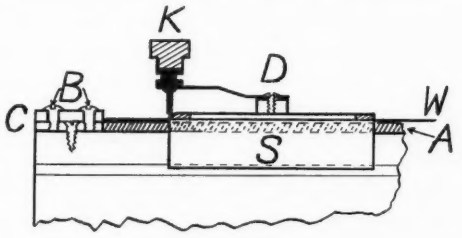


FIGURE 2
A—Oak strip; *B*—Screws; *C*—Clamp; *D*—Pivot of key *K*; *K*—Key; *S*—Slider; *W*—Slide wire.

The H-shaped standard Weston cell is mounted in mercury cups, made by drilling holes into a block of wood and paraffining the inside to prevent the escape of the mercury. The cell can readily be removed for demonstration purposes and as easily replaced.

The half-cells are made of pyrex glass as shown in Figure 3. The siphon tubes are filled with a 1% solution of agar, 1 N in KNO_3. (This is poured in hot and solidifies in a short time.) 1 N KNO_3, in a flat culture dish into which the siphon tubes dip, completes the salt bridge. KNO_3, instead of KCl, was used to avoid precipitation with Ag^+ and Pb^{++}. The electrodes are made from strips of metal (M) soldered to copper lead wires (L), which are sealed into rubber stoppers with wax.

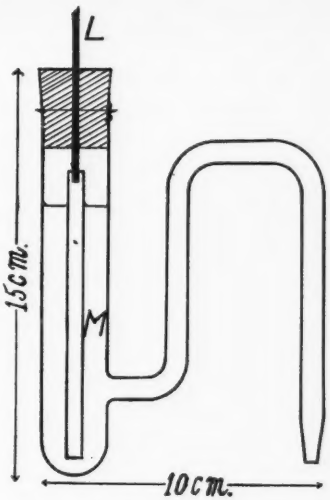


FIGURE 3
M—Metal electrode
L—Copper lead wires

The cells slip easily into a simple wooden stand (Figure 4) which holds them rigid. Electrical connection is made through mercury cups (marked + and −) into which the copper lead wires dip. Any cell combination can thus be assembled in a moment. When not in use, the half-cells are kept in a rack made like the stand but with openings for six half-cells.

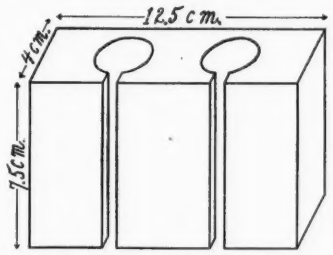


FIGURE 4.—HALF-CELL HOLDER

Lecture Presentation

Before explaining the operation of the instrument, a few definitions are given. The *ohm* is defined as the resistance offered by a standard column of mercury; the ampere, as current flowing at the rate of one coulomb per second. (The coulomb is already familiar to the student as $^1/_{96,500}$ of the quantity of electricity required to deposit one gram-equivalent of an element.) The volt is then defined by means of Ohm's law, $E = IR$.

Connecting the working cell by closing the switch at the upper left-hand corner gives, along the slide wire, a uniform potential drop, the total value of which is controlled by the rheostat in the upper right-hand corner. The slider is set at 1.018 v., the potential of the standard cell, to which connection is now made by means of the double-throw switch. The tapping key is then depressed and the rheostat adjusted until there is no galvanometer deflection. This means that no current is flowing in the

standard cell circuit. Hence the potential drop in the battery circuit along this portion of the slide wire exactly equals that of the standard cell which it opposes. The potential drop is 1 centivolt per centimeter, and the scale direct-reading. We are now ready to measure the e. m. f. of an unknown cell.

Since the electromotive series of the elements is familiar to all elementary students, we first show how the numerical values of the reduction potentials are obtained. Any cell combination gives a *difference in potential* which we can measure by means of the potentiometer. This may be compared to the difference in altitude between two places. There is no *absolute* scale of altitudes and no *absolute* scale of potentials. In one case, we agree to call mean sea level the zero of our scale; in the other, the potential of hydrogen gas (at one atmosphere pressure) against hydrogen ion (at one molal activity). The difference between ion *activity* and solute *concentration* is of course pointed out.

A hydrogen electrode is then shown and explained and the *molal* reduction potential of several metals is measured. Using ordinary cylinder hydrogen, "C.P." metals, and laboratory distilled water, it is easy to come within about a centivolt of the accepted values for the common metals. Zn, Pb, Cu, and Ag are particularly good. The half cells are made up with solutions 1 *M* in the metal ion and these are connected in turn against the hydrogen half cell. The *sign* of the reduction potential is taken as that of the *solution*. This rather troublesome convention is discussed at some length. We then show how different half-cells may be connected together and the e. m. f. of the combination calculated from the algebraic difference of the two molal reduction potentials (again like altitudes).

The method of representing cells is explained, together with the ionic equilibria which are represented by them. The *sign* of the e. m. f. of the cell tells us the *direction* in which the reaction tends to go. Thus the cell

$$Cu \mid Cu^{++}\,(1M) \parallel Ag^{+}\,(1M) \mid Ag$$

represents the equilibrium

$$\tfrac{1}{2}Cu + Ag^{+} \rightleftharpoons \tfrac{1}{2}Cu^{++} + Ag$$

Since the molal reduction potentials of $Cu \mid Cu^{++}$ is -0.34 v. and of $Ag \mid Ag^{+}$ is -0.80 v., the e. m. f. of the cell;

$$\begin{aligned} E\ (\text{cell}) &= -0.34 - (-0.80) \\ &= +\ 0.46\ \text{v.} \end{aligned}$$

The positive sign of the cell shows that under the specified conditions, the reaction tends to go from left to right and copper tends to displace silver.

The principle can be generalized and applied to negative as well as positive ions. If the sign of the cell is *positive*, the reaction will give

oxidation in the *left* half-cell and *reduction* in the *right*. The fact that both *right* and *reduction* have the same initial letter gives a useful mnemonic key. If the sign of the cell is *negative*, reduction goes on in the left half-cell and oxidation in the right.

The Effect of Ionic Concentration

The student is already familiar with the effect of a common ion upon the solubility of a salt. Might not ion activity similarly affect reduction potentials? According to Nernst's kinetic picture of the balanced forces at an electrode, the tendency of the electrode to dissolve as ions is opposed by the electromotive force set up between ions and electrode and also by the osmotic pressure of the ions already in solution.

$$\text{Solution pressure} = \text{E. m. f.} + \text{Osmotic pressure.}$$

Thermodynamics shows that these terms can be evaluated and that the measured electromotive force

$$E = E_1 - \frac{RT}{nF} \ln C \tag{1}$$

Substituting the values of the gas constant (R), Faraday's equivalent (F), and the absolute temperature (T), and changing from natural to common logarithms gives, at 20°C.

$$E = E_1 - \frac{0.06}{n} \log C \tag{2}$$

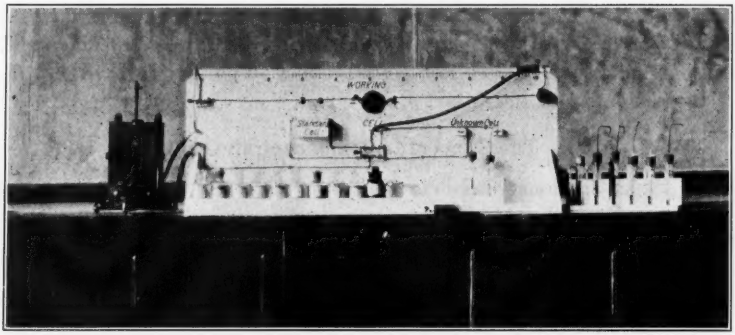
Here (n) represents the *change in valence of* (number of electrons lost by) each substance in going from the reduced to the oxidized state, while (C) represents the molal activity of the corresponding ion. If $C = 1$, $\log C = 0$ and

$$E = E_1 \tag{3}$$

E_1 is therefore a *constant*, characteristic of the electrode. It is called the *molal reduction potential* and is the e. m. f. between an electrode and a solution $1M$ in the ions furnished by it. According to Nernst's theory, it is a measure of the *solution pressure* of the substance which is ionizing.

The quantitative effect of changing the concentration of the ions is then illustrated by a number of examples. Two identical half-cells are first connected and a zero difference in potential predicted and found. The solution in one half-cell is then diluted in stages, by putting a known amount of it into a volumetric flask which is filled to the mark with distilled water. The following series of cells is set up and the measured e. m. f. compared with that calculated. In such concentration cells, of course, the actual value of the reduction potential need not be known.

$$\text{Ag} \mid \text{Ag}^+(1M) \parallel \text{Ag}^+(1M) \mid \text{Ag}. \quad \text{E. m. f. (observed)} = 0.00 \text{ v.}$$
$$\text{E. m. f. (calculated)} = (E_1 - E_1) = 0.00 \text{ v.}$$



POTENTIOMETER SET-UP

$$\mathrm{Ag}\,|\,\mathrm{Ag^+}(0.1M)\,||\,\mathrm{Ag^+}(1M)\,|\,\mathrm{Ag}. \quad \text{E. m. f. (observed)} = +0.06 \text{ v.}$$
$$\text{E. m. f. (calculated)} = (E_1 - (0.06/1)\log(10^{-1})) - E_1 = (-0.06)(-1) = +0.06 \text{ v.}$$

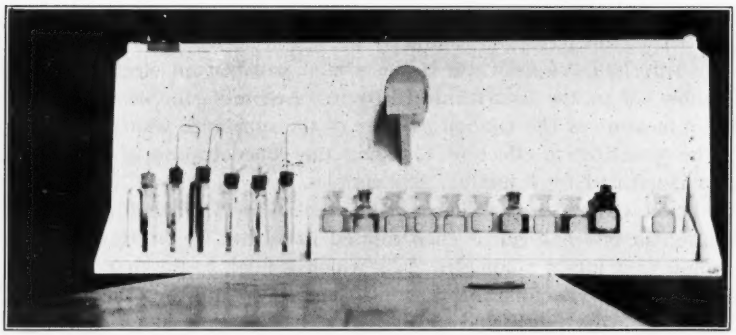
$$\mathrm{Ag}\,|\,\mathrm{Ag^+}(0.001M)\,||\,\mathrm{Ag^+}(1M)\,|\,\mathrm{Ag}. \quad \text{E. m. f. (observed)} = +0.17 \text{ v.}$$
$$\text{E. m. f. (calculated)} = +0.18 \text{ v.}$$

A similar set of experiments with Cu^{++} cells shows that in this case the change is only $0.06 \div 2$ or 0.03 v. for each tenfold change in ion activity. These experiments give a very clear and convincing proof of the Nernst equation.

We can now answer such questions as "How completely will metallic iron precipate copper from a solution, if at the end of the reaction $[Fe^{++}] = 1M$?" Consider the cell

$$\mathrm{Fe}\,|\,\mathrm{Fe^{++}}\ (1M)\,||\,\mathrm{Cu^{++}}\ (cM)\,|\,\mathrm{Cu}$$

The molal reduction potentials are $\mathrm{Fe}\,|\,\mathrm{Fe^{++}} = +0.44$ v.; $\mathrm{Cu}\,|\,\mathrm{Cu^{++}} = -0.34$ v., hence the e. m. f. of the cell is given by the equation



BACK OF POTENTIOMETER, SHOWING WORKING CELL SHELF

The racks for half-cells and for solutions of electrolytes fit here conveniently when not in use.

$$E \text{ (cell)} = +0.44-(-0.34-0.03 \log [Cu^{++}])$$

As the concentration of the Cu^{++} is reduced, its reduction potential will be increased. Finally the e. m. f. of the whole cell will be reduced to zero, when no further reaction will occur. Putting E (cell) = 0 gives

$$0.03 \log [Cu^{++}] = -0.78$$
$$\log [Cu^{++}] = -26, \text{ hence}$$
$$[Cu^{++}] = 10^{-26} \text{ mols./l.}$$

This shows the copper will be "completely" precipitated under the circumstances (practically those obtaining in the laboratory when copper ions are removed before precipitating Cd as the yellow CdS). A similar calculation shows that Cd, with a molal reduction potential of +0.40 v. will not be precipitated unless it is present at a greater concentration than 0.05 M (which corresponds to about 300 mg. of Cd, 70% ionized, in the volume of 40 cc.).

Oxidizing and Reducing Substances in Solution

Hitherto we have considered the e. m. f. of half-cells consisting of a neutral substance and an ion. The same substance may also exist in solution in two different states of oxidation. If we put an inert conductor (like a platinum wire) into a solution containing a mixture of Fe^{++} and Fe^{+++}, we find between wire and solution a difference in potential, the magnitude of which, in a solution of constant H^+ activity, depends on the ratio between the two ion concentrations. Such a system may therefore form a half-cell. The following cell

$$Pt \mid \frac{Fe^{+++}\ (1M)}{Fe^{++}\ (1M)} \parallel H^+(1M) \mid H_2 \text{ (gas, 1 at.)}$$

we find has an e. m. f. of −0.75 v. Hence under these conditions the reaction

$$Fe^{++} + H^+ \rightleftharpoons Fe^{+++} + {}^1/_2H_2$$

will tend to go to the left; Fe^{+++} oxidizing H_2. The actual reduction potential of the ferrous-ferric half-cell is dependent not on the particular concentration of either ion, but on the *ratio* of the two concentrations. In general, for such a half-cell,

$$E = E_1 - \frac{0.06}{n} \log \frac{[\text{oxidized}]}{[\text{reduced}]}$$

where n is now the *difference in valence* between the two states.

We are now in a position to deal, experimentally and theoretically, with any reversible ionic oxidation-reduction reaction. For example, in which direction will the following reaction proceed?

$$Ag + Fe^{+++} \rightleftharpoons Ag^+ + Fe^{++}$$

Set up the corresponding cell

$$\mathrm{Pt} \mid \frac{\mathrm{Fe^{+++}}\ (1M)}{\mathrm{Fe^{++}}\ (1M)} \parallel \mathrm{Ag^{+}}(1M) \mid \mathrm{Ag}$$

The E (cell) is calculated and found to be +0.05 v.

$$\text{E. m. f. (cell)} = -0.75-(-0.80) = +0.05 \text{ v.}$$

Therefore, in a solution molal in all three ions *Ag^+ oxidizes Fe^{++}*. However, the potential of the cell is small and if the Ag^+ were reduced to 0.1 M or the $Fe^{+++} \mid Fe^{++}$ ratio increased to 10, the reaction would tend to go the other way. *Ag then reduces Fe^{+++}*. This is strikingly illustrated by an experiment shown by A. A. Noyes in the course of the lecture to which reference has already been made. In one test tube, $Fe(NO_3)_2$ (1 M) slowly precipitates silver from $AgNO_3$ (1 M) and becomes colored. In a second test tube, powdered silver slowly decolorizes $Fe(SCN)_3$, reducing Fe^{+++} to Fe^{++}, because the concentration of Ag^+ from the insoluble AgSCN is kept very low.

The (algebraic) increase in the reduction potential caused by insolubility of a compound of the higher state of oxidation explains why it is sometimes possible to oxidize a substance which is usually unaffected by even the strongest oxidizing agents. Thus, the value of the molal reduction potential of $Co^{++} \mid Co^{+++}$ is -1.98 v. (as compared with -1.39 v. for such a strong oxidizing agent as chlorine). Accordingly, only in forming such insoluble compounds as $Co(OH)_3$ and $K_3Co(NO_2)_6$, which furnish an extremely low concentration of Co^{+++}, do we obtain cobalt in the higher valence.

Finally, the potentiometer gives a simple method of determining the solubility of "insoluble" substances, as the following experiment shows. AgCl is precipitated, washed free of excess ions, shaken with distilled water, and stored in a dark bottle. We then set up the cell:

$$\mathrm{Ag} \mid \mathrm{Ag^{+}}\ (\text{in sat. AgCl}) \parallel \mathrm{Ag^{+}}(1M) \mid \mathrm{Ag}$$

The e. m. f. is found to be +0.30 v. Calculation shows

$$(E_1 - 0.06\ \log[\mathrm{Ag^{+}}]) - E_1 = +0.30, \text{ therefore}$$
$$\mathrm{Log}[\mathrm{Ag^{+}}] = -5 \text{ and } [\mathrm{Ag^{+}}] = 10^{-5} \text{ mols./l.}$$

Assuming complete dissociation, this figure represents the solubility of AgCl. In similar fashion, the solubility of $PbCl_2$ can also be demonstrated.

Conclusion

We have described the construction of a simple, semi-diagrammatic potentiometer suitable for lecture demonstration before a large class. The electrical circuits and the readings of the scale can both be seen clearly. Using this instrument and the simple half-cells also described, it is pos-

sible to demonstrate the molal reduction potentials of the commoner metals, obtaining values within one or two centivolts of the accepted ones.

We have briefly outlined our presentation of the theory of the potentiometer and of the reactions at a reversible electrode. The correctness of Nernst's equation showing the effect of changing ionic concentration upon the reduction potential is demonstrated by many simple experiments with concentration cells.

Finally, we have shown the importance of an early understanding of oxidation-reduction reactions and some of the applications of the theory in the field of qualitative analysis, including the determination of the solubility of "insoluble" compounds.

Peanuts: Elephant Food. Although a native of tropical America, shown by excavations of prehistoric remains in Peru, the peanut was introduced into our Southern states in slave-trading times, having been carried to Africa by early explorers....

Biological chemists have discovered that the peanut has a large percentage of digestible protein and fat, and that the nut contains the water-soluble and fat-soluble vitamins which are so necessary for a normal diet. It has been shown that refined peanut oil is one of the best of the salad oils, and that the less refined pressings are well adapted to soap manufacture. Commercial research has developed merchandising methods, designing appropriate containers for shelled and salted nuts for peanut confections and other products sold in small packages at retail; and the advertising expert has invented suitable publicity, even going so far as to prepare appropriate slogans. The household research workers have developed a number of new dishes in which peanut products are featured....

All of these activities have resulted in the establishment of the peanut-growing industry as one of the important farming industries of the South. The peanut is a good cash crop, as it is not only comparatively immune to pests, but as a result of its ability to fix nitrogen from the atmosphere, it requires less fertilizer than many other crops. In the year 1928, about 400,000 tons of peanuts were harvested, and an additional quantity was "hogged off" by turning swine into the fields of mature plants....

A recent peanut product, the result of chemical research, is a flour, so-called, which, mixed in proper proportions with wheat flour, gives a bread or cake which contains a large proportion of digestible protein. This flour is usually made from the cake remaining after expressing the oil from the shelled and blanched nuts. The flour is recommended for use in the diet of diabetic patients, as it contains only a small proportion of sugars.

The chemist of one of the Southern experiment stations is said to have developed from the peanut, its stalks, shells, and skins, some 264 different products.

The ordinary diet of the poorer classes in the Southern states is deficient in digestible protein and in vitamins. Attempts are now being made to improve this diet by introducing the use of milk and green vegetables....It would seem that the peanut and the soy bean, both of which by proper treatment yield a flour rich in digestible protein and vitamins, might be adapted to use as a supplement to this deficient diet, with the result that these poor people might be freed from the diseases due to malnutrition.

The peanut industry has evolved from its original status, where it ranked with the popcorn industry, into a well-organized business on modern lines.—*Ind. Bull. of Arthur D. Little, Inc.*

AN APPARATUS FOR DEMONSTRATING SOME TRANSFORMATIONS OF ENERGY

F. E. Holmes and A. O. Snoddy, Cincinnati, Ohio

Several modifications of an apparatus are described which derive heat energy from their environment and dissipate it as latent heat in water vapor. Visible work is done. It is suggested that they may be used in high-school science classes to demonstrate the energy changes and the resulting differences in vapor pressure and hydrostatic pressure upon which their activity depends.

. . . . . .

The fascinating feature of the little heat engines described below is their obvious activity without any apparent source of energy. Besides being amusing curiosities, they illustrate several physical phenomena encountered elsewhere in the laboratory and in industry. It has occurred to us that they may be useful in high-school classes in demonstrating these phenomena, the more so because they stimulate spontaneous interest and curiosity as to why they behave as they do.

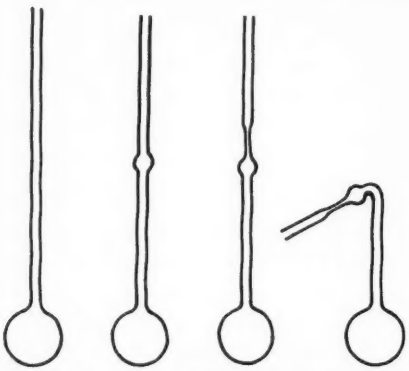


Figure 1.—Steps in Making the Simpler Apparatus

All the forms of apparatus described here consist essentially of a lower and upper chamber communicating through one or two tubes. By exhausting the air, the space not occupied by the volatile liquid is filled with its vapor. Heat from the air and reradiated from nearby objects enters all parts of the apparatus. That absorbed by the wet wick surrounding the upper bulb is, however, used up in evaporating water. Because of the low temperature resulting from this evaporation, energy is absorbed from the vapor in the upper chamber reducing its pressure and condensing much of it to liquid again.

The difference in pressure between vapor in the lower bulb and that in the upper due to their difference in temperature is balanced by the hydrostatic pressure of liquid in the connecting tubes. The pressure and volume of gas in the lower bulb increase, expelling liquid from the lower bulb into the upper until finally gas escapes into the tube connecting the two chambers. A cycle is now established that may be maintained as long as the difference in temperature can be maintained.

We designed the types of apparatus containing fountains or wheels to demonstrate more forcefully and obviously, by visible work done, the

considerable amount of energy passing through them. In the simplest form of apparatus, the stream of bubbles and the return flow of liquid were in the same tube. By separating them in two tubes, the considerable difference in hydrostatic pressure between the all-liquid column and the gas plus liquid column of the same height could be obtained at the orifice of a nozzle. Flow of liquid, of course, resulted. This is the same phenomenon, the gas lift, that is used to raise oil or water from wells and to circulate water in the humble coffee percolator.

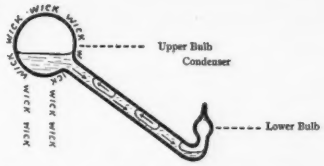


FIGURE 2.—THE SIMPLER APPARATUS IN OPERATION
The water reservoir, a bottle, is not shown.

The instructor may elaborate on the simple explanation of the energy changes involved to whatever extent best suits his purpose.

An excellent opportunity is presented to refute again the ancient idea of "perpetual motion." Many students will see in this apparatus an example of self-sustained activity. As the discussion reveals the source of energy, they will see that their first impression was wrong. We suggest demonstrating this dependence upon outside temperature, at the same time showing the effect of temperature on vapor pressure, by the following experiments: (1) warming or cooling the lower bulb, (2) replacing the wet wick with a dry one and vice versa, (3) placing the apparatus with wet and dry bulb thermometers in dry or humid atmospheres, in still air, or in the draft from a fan or open window.

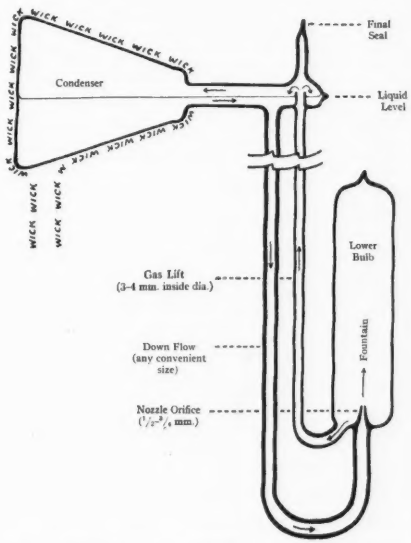


FIGURE 3.—SIMPLER FORM OF FOUNTAIN AND GAS LIFT

The simplest form of apparatus, often seen in opticians' windows, is made from a tube of from 3 to 5 mm. inside diameter and of a length of about 12 cm. At one end of this tube, a bulb of 5 to 10 cc. capacity is blown. About 6 cm. from this, a small bulb of about 1 cc. capacity is formed. Beyond this, the tube is constricted by drawing it

out to about one-third its original diameter. At this point, it will be sealed off later. The tube is next bent at right angles near the small bulb on the side toward the larger bulb.

When the tube has cooled, the whole system is filled with ethyl ether or some other liquid which has a high vapor pressure at room temperature. The open end of the tube is then attached to a vacuum pump—the ordinary water jet pump will suffice—and the air and excess liquid are expelled by gentle boiling under reduced pressure. It is convenient to place a screw clamp on the rubber hose to the pump, to be closed occasionally when one wishes to find out whether the volume of liquid is about right. The liquid should just flow out of the larger bulb and fill the tube when it is tipped to the desired angle, leaving the smaller bulb and at least half of the larger bulb filled with vapor. The tube is again returned to a position in which the liquid flows into the large bulb and is sealed off with the pinch clamp open and the pump in operation.

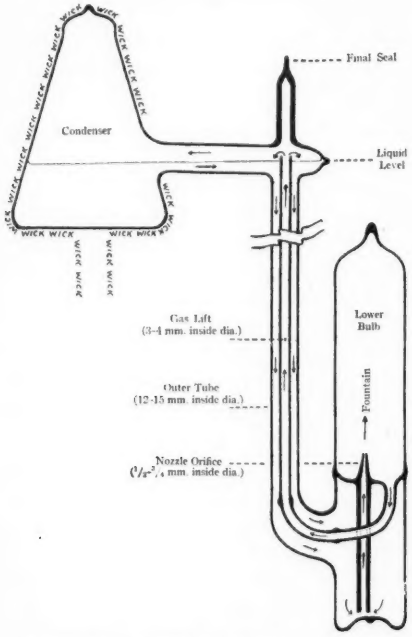


FIGURE 4.—FOUNTAIN HAVING GAS LIFT INSIDE DOWN-FLOW TUBE

Some will prefer to leave the rubber tube in place and close the end with a clamp after evacuating instead of sealing off, in order that the liquid may be easily replaced by another or the partial vacuum renewed at will.

The steps in making the simpler apparatus are shown in Figures 1 and 2.

The desirability of using a screw clamp instead of sealing off is greater in the more complex apparatus. In these forms it is difficult to obtain perfectly air-tight seals. If the seals are not absolutely free of leaks, renewal of the partial vacuum at intervals of a week or two is necessary. Closing with a rubber tube and clamp is also desirable because of the greater opportunity afforded by these forms for observing and comparing the behavior of various volatile liquids, or the effect on vapor pressure of two miscible or immiscible liquids.

If a vacuum pump is not available, the air may be replaced by vapor of the liquid used by boiling on the steam-bath, using a rubber tube and clamp as above, cooling and sealing off, if a permanent seal is desired, with the clamp closed.

The more complex forms of apparatus are illustrated by Figures 3, 4, 5, and 6. Specifications are given in the labeling of the parts. Those who have enough experience in glass blowing to attempt these little engines will have their own methods of accomplishing their construction.

Because of the number of seals close together, we have found it desirable to use pyrex glass.

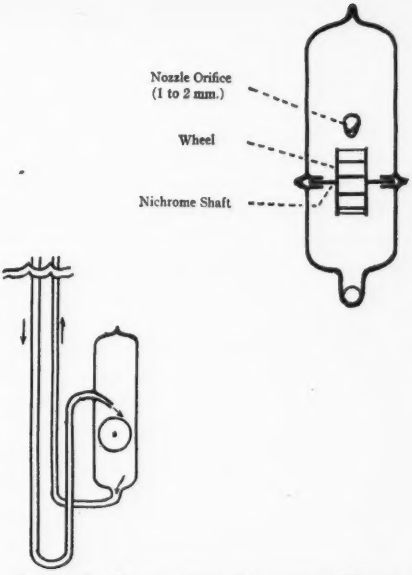


FIGURE 5.—LOWER BULB CONTAINING WHEEL; AND ARRANGEMENT OF GAS LIFT AND DOWN FLOW

To those of an experimental turn of mind, additional modifications will doubtless occur. Cataracts, ornamental fountains, springs of colored ether rising through water, or cataracts of colored carbon tetrachloride falling through water, fountains that change color from that of ether and iodine or Sudan III to that of clear water alternately, and fountains illuminated from below are among the variations that are possible.

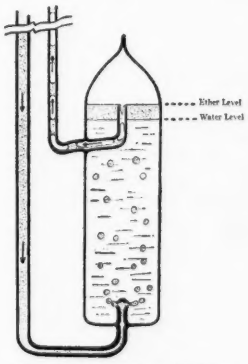


FIGURE 6.—THE ETHER SPRING IN WATER

Any one of a number of liquids may be used. Ethyl ether shows the most vigorous action of those we have tried. Ether operates well when the "lift" is as great as 18 cm. Carbon tetrachloride will operate well if the lift is about 12 cm. Other liquids that have been used are chloroform, alcohol, carbon bisulfide, and low-boiling petroleum ether. Water alone was not satisfactory in our apparatus.

The liquids may be colored to show the bubbles and fountain more clearly as well as to make a more attractive appearance. Iodine gives an orange to brown color to its solu-

tion in ethyl ether, and beautiful shades of violet or purple in carbon tetrachloride or chloroform. Sudan III colors both ether and carbon tetrachloride red. Many standard bacteriological stains may be used in alcohol or water. Fluorescein in water and Sudan III in ether make a beautiful and striking contrast in the fountain of alternate colors.

The wick is of any absorbent cloth, such as that from which hand towels are made. It dips into an ordinary bottle filled with water, which is drawn up by capillary action into the wick as fast as it evaporates from the exposed portions.

Our Insect Foes and Allies. When agriculture was first attempted on the American basis in Hawaii, insects which previously had been unnoticed began to thrive mightily on the imported sugar cane..... Some ninety types of insects have been introduced into Hawaii to keep in check native insects of all kinds which tended to go out of bounds when fed on new imported crops.....

Numbers of very interesting, and at times thrilling victories have been scored by the entomologist. One of the most notable, perhaps, was that over a type of moth which came apparently from nowhere to attack the native cocoanut palms of Fiji. No native parasite existed, and for some years extensive damage was done. In this case, the search was for enemies of insects related to the pest (Levuana iridescens) which existed in other islands of the Pacific. Fortunately, a fly was found which attacked a caterpillar related to Levuana, and which, when released in Fiji, soon brought the pest under control.

Fighting pests with parasites is not always simple. Sometimes a native species either attacks the newcomer, or else plays "dog in the manger" and acts as a restricting competitor. Also, two newcomers may restrict each other. In the recent case of the Mediterranean fruit fly which came into our Southern States, the chief difficulty was that the fruit fly was able to lay its eggs inside of thick-skinned oranges, where its young could develop out of reach of nearly every available insect enemy or chemical. It proved possible in this case to stamp the pest out by military sternness and the situation was eventually saved.

Occasionally, a native insect will change its taste, and go from a weed to a cultivated crop. Sometimes weeds can be fostered which will eventually win the insect from the cultivated crop. Also certain varieties of crop plant can be found which are resistant to a particular insect either because it is distasteful, or because it lacks favorable taste. The entire crop and pest situation is complicated and curiously interrelated, and, what is more, it is plastic and forever changing.

By combination of poison sprays, rigid exclusion, weed eradication (or encouragement), the good offices of birds, and occasionally, rare good luck, along with present insect parasitic control, it is possible to keep insects from getting the upper hand over man.

The cheapest and probably the ideal method for keeping insects in check is with other insects, themselves unobjectionable to man. Much more work is to be expected along this line until the ultimate is reached where in every land all possible types of insects which can stand the climate are present, in a big melting pot, to stand guard over each other, and in that way to assist man. In the meantime, at least, constant vigilance and plenty of chemical insecticide are necessary.—*Ind. Bull. of Arthur D. Little, Inc.*

A LABORATORY REPRODUCTION OF THE VISCOSE PROCESS

HOWARD JAMES, UNIVERSITY OF COLORADO, BOULDER, COLORADO

A laboratory process for the preparation of rayon is described. The process follows the commercial method faithfully in the major details. Only commonplace chemicals and apparatus are required.

. . . . . .

The viscose process for the production of rayon, in addition to its being the most important commercially, is, perhaps, the most interesting from the standpoint of the reactions involved. These reactions are, in the main, the formation of the mono-sodium ester of cellulose, the subsequent formation of the sodium xanthogenate, or sodium xanthate, and finally the conversion of the xanthate back to cellulose.

The laboratory process described here is built around these three reactions, and follows the commercial process faithfully in its major details. The chemicals used are commonplace, and the apparatus is easily assembled. Furthermore, since there is no point to an attempt to equal the commercial product in the quality of the viscose silk, rigid control of humidity and temperature is unnecessary. If normal room temperature, or slightly below, is maintained throughout the experiment, the results should be satisfactory.

Experimental

Immerse a highly porous filter paper (cellulose) of about 7 cm. diameter in a 20% aqueous solution of sodium hydroxide. The mercerizing which takes place in the solution will require about three hours, and will result in the formation of the sodium complex, $[2(C_6H_{10}O_5)_x]\cdot x\text{NaOH}$. After sufficient time has elapsed, remove the mercerized paper from the caustic and press it as dry as possible with a spatula. Tear the paper into small crumbs, and place them immediately into a wide-mouth bottle (50 cc. capacity). Allow the crumbs to age for thirty-six hours in the tightly stoppered bottle.

Proper conditions of humidity are very important in the aging, or ripening process. If the mercerized cellulose is dried between filter papers or by exposure to air before it is allowed to age, the resulting product will form either an inferior grade of viscose or none at all.

After the crumbs have ripened, transfer them to a test tube, add 3 to 5 cc. of carbon bisulfide, and cork the tube tightly (do not use a rubber stopper). Within two or three days the formation of the xanthate should be complete. The crumbs have now swelled up, become rubbery and gelatinous, and orange-brown in color. The reaction which has occurred may be represented as follows:

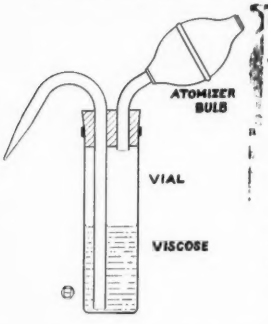
$$[2(C_6H_{10}O_5)_x]\cdot x\text{NaOH} + x\text{CS}_2 \longrightarrow [(C_6H_{10}O_5)_2\cdot\text{C}\cdot\text{S}\cdot\text{S}\cdot\text{Na}]_x$$

Remove the excess carbon bisulfide, pressing as much of the liquid out of

the crumbs as possible with a glass rod, and allow the tube to remain open for a few minutes. Then add 5 to 6 cc. of 5% sodium hydroxide solution and again stopper the tube. The formation of the viscose will require from two to three days.

After its formation is complete, the viscose, which is a colloidal emulsoid dispersion of sodium xanthate in sodium hydroxide solution, must be aged for two days. During this aging process, the viscosity of the solution decreases and reaches a minimum after about two days. The viscose is then ready to be spun.

The details of the spinning apparatus are given by the illustration.



From this wash-bottle-like affair the viscose is to be spun into a hardening bath consisting of a solution of 12% sulfuric acid and 4% sodium sulfate in water. Proceed as follows: pour the hardening bath into a shallow glass dish, such as a small developing tray. Place the nozzle of the spinner just below the surface of the hardener, and force the viscose into the bath by gently pressing the bulb. Cause the flow of viscose to be as even as possible, and move the nozzle about in the solution to prevent tangling of the thread. The crude "silk" forms as a glistening, light yellow, somewhat hollow thread. Wash it thoroughly in warm, soapy water, then rinse with pure warm water.

The crude viscose silk contains some free sulfur which can, if it is desired to continue the purification, be removed by immersing the thread for twenty minutes at 70°C. in a solution of four parts sodium sulfide in one thousand parts water. At the end of this time, remove the thread, wash it, and bleach it with chlorine or 3% hydrogen peroxide. After the bleaching is complete, wash the silk with soapy water, then pure water, and allow it to dry.

Seeds of Rubber Tree Yield Valuable Oil. The rubber planters of the Dutch East Indies, with profits depressed by the present low price of rubber, are seeking to recoup by extracting oil from seeds of the Para rubber tree. An item in the German scientific journal, *Die Umschau*, states that rubber-seed oil has in considerable measure the drying properties that make linseed oil valuable, and that it can compete to advantage with linseed oil, because it is at present about 20 to 25 per cent cheaper. It is used in the manufacture of paint, linoleum and soap.

Hevea, the Para rubber tree, is a botanical cousin of the castor bean, whose seed has long been a source of a widely used oil. Rubber seed oil-cake cannot be used for cattle feed because it is poisonous. The planters, therefore, burn it under their boilers. Gathering the seed for pressing in the Dutch East Indies is made practicable through the low labor costs.—*Science Service*

A SIMPLE WATER-MOTOR

MOWBRAY RITCHIE, THE UNIVERSITY, EDINBURGH, SCOTLAND

The water-motor here described has been found suitable as a means of stirring when the power required is not too large. It can be quickly constructed, and uses in working only a small amount of water.

The apparatus consists essentially of two parts. Water under pressure passes through the glass tube *A* (see Figure 1), and, emerging from four narrow jets, strikes tangentially the inside surface of the half-flask *B*. A plan of the jet system is given in Figure 2. The half-flask *B* is free to rotate, and is supported by the glass tube *C* which passes tightly through the rubber stopper *D*, and to which is attached the cork pulley wheel *E*. This rotating part is supported by an outer glass tube *F*, held rigidly by a clamp; two metal washers below the pulley-wheel provide the necessary bearing surfaces. The side tube *M* is employed for the addition of lubricating oil. A convenient diameter of the rotating part *B* at its widest part is four to five inches; the jets when in position are about a quarter of an inch from the sides.

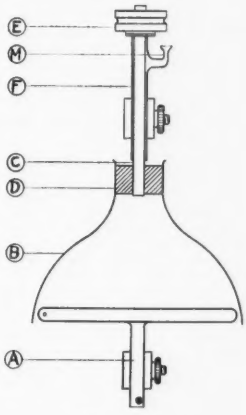


FIGURE 1

To prevent splashing, the lower part of the apparatus is best surrounded by some sort of cover. If desired, the stationary entry tube, carrying the water to the jets, may be placed inside the rotating tube carrying the pulley wheel. The water then enters at the top, and passes downward to the jets. The diameters of the three concentric tubes must, of course, be suitably chosen for the tubes to fit each other fairly closely. Such a model, provided with a suitable cover and exit tube (constructed from larger half-flask) has been in use for a considerable time, and has given no trouble. Such a cover is best placed so that the entrance to the exit tube is not directly below the jet system; the swirl, imparted to the waste water causes the water to climb up the sides of the cover, and, if not removed, to interfere with the motion of the rotator.

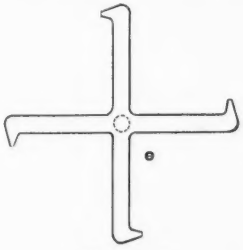


FIGURE 2

For most purposes, some kind of reduction gear must be employed.

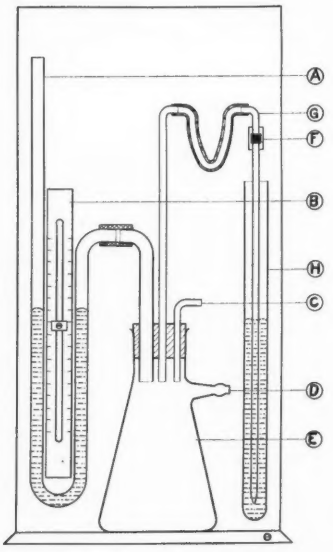
Doing easily what others find difficult is talent; doing what is impossible for talent is genius.—AMIEL

A PRESSURE REGULATOR FOR DISTILLATIONS

CHARLES B. DEWITT, UNIVERSITY OF COLORADO, BOULDER, COLORADO

In the identification of organic liquids, the determination of the boiling points is nearly always one of the first procedures, but the value of this determination is markedly decreased if the local barometric pressure is not very close to 760 mm. The pressure regulator here described makes possible the distillation of a liquid under standard pressure and eliminates the necessity for making the usual allowances when comparing observed boiling points with those recorded in the literature. The regulator is made entirely from materials that are to be found in any laboratory. It is compact, easy to use, and above all accurate.

The materials needed are: a ring stand with a flat base, a board 1″ × 6″ × 18,″ a filter flask, a millimeter scale, a spring clip, some glass tubing in six-, eight-, and twelve-millimeter sizes, rubber tubing, some thin metal strips, and a buret clamp.



The board is drilled with a one-inch hole about seven inches from one end, and is fastened to the ring stand with metal strips around the upright and under the base. A buret clamp attached to the upright rod projects through the hole and holds the filter flask *E* which is fitted with a three-hole rubber stopper carrying the tubes shown in the drawing. This stopper is held in place by a metal strip passing over the top and fastened by the arms of the buret clamp. *A* is an open-end mercury manometer made from eight-millimeter tubing. The millimeter scale *B* is slotted as shown and held in place by a screw and light spring strip. *F*, *G*, and *H* constitute the relief valve which maintains pressure at a constant level. *H* is a thick-walled twelve-millimeter tube filled with mercury as shown by shading, and loosely stoppered with glass wool. The small tube *G* is drawn to a capillary of about one millimeter bore at the lower end, and is connected to the tube from *E* with a rubber tube long enough to allow several inches vertical adjustment. *F* is a large-size spring-clip battery connector for holding tube *G* at any desired height.

For use, the side tube *D* of the filter flask is connected to the receiver of the distilling apparatus, and tube *C* is connected to a compressed air line. When air is turned on, the pressure inside the apparatus can in-

crease till just sufficient to overcome the head of mercury in *H*. Adjustment is made by raising or lowering *G* till the reading of the manometer added to the barometric reading equals 760 mm. With a very slow but steady current of air bubbling through *H*, standard pressure can be maintained with a deviation of not more than one millimeter.

In the first model of this regulator built by the writer, an ordinary barometer was used instead of the open manometer, but the latter has proved far more convenient.

Color Finishes on Aluminum. The familiar bluish silver surface of aluminum may now be changed to any one of many shades of color by the use of chemical baths or electrochemical treatments.....Aluminum, itself a durable metal, has found in its own oxide a coating that not only allows various color finishes, but is tenacious and stable. Aluminum oxide is pure white, but when a coating is produced on commercial aluminum or its alloys, color is imparted by the minute particles of impurities or alloying constituents in the parent metal.

Thus, by treatment in a solution of certain chemical salts carefully controlled, aluminum shingles are given a durable enamel-like coating of any desired shade of gray. Brown shades may be obtained in a similar manner.

Oxide coatings are also produced electrochemically when the aluminum article is made the anode in a suitable solution. This anodic treatment....has become known in architectural foundries as "deplating." The finish is often used when exterior ornamental castings of aluminum require toning, and on aluminum-silicon alloys grays may be produced so dark as to approach black.....Anodic oxidation in chromic acid produces a coating of high corrosion-resistance widely used on aircraft parts of the duralumin-type alloys.

The same anodic coating method, using a special solution, produces an oxide film with strong affinity for certain types of organic dyes. The coating may be dyed in an almost infinite variety of colors.....Aside from color, the coating is hard and abrasion-resistant, resembling the crystallized form of aluminum oxide, corundum.....

The surface texture of the dyed oxide finish varies with the texture of the metal before treatment—polished aluminum produces a smooth enamel-like finish; etched or even sand-blasted metal imparts a matte surface to the dyed film of oxide. These finishes may be waxed or lacquered. For outdoor service a type of oxide coating is under development to permit tinting with mineral colors. Indoors, the more stable organic dyes are quite free from fading troubles, but they cannot as yet be recommended for general outdoor use.

Paints, enamels, and lacquers are often used as a finish for many classes of aluminum articles. The development of oxide film coatings has come independently and not because of there being any difficulty in applying enamels or lacquers.

Aluminum may be electroplated with another metal to supply a desired harmony or contrast in an assembly of metals. Aluminum may be plated with nickel, chromium, gold, silver, copper, zinc, brass, etc. Approximately five million chromium-plated hub-caps for automobile wheels are now in service.

With each of the finishes—plated, oxide coated, painted, enameled, or lacquered—colored areas may be used in conjunction with bare aluminum surfaces, matte or polished, to give pleasing contrast or to accentuate design.—*Ind. Bull. of Arthur D. Little, Inc.*

A STOPCOCK REMOVER

CHARLES E. BISH, WESTERN HIGH SCHOOL, WASHINGTON, D. C.

This laboratory mechanism has for its purpose the solving of the frozen stopcock problem. The method described here will be found particularly useful when the more common and less drastic methods fail.

Two blocks of soft wood 1″ × 3″ × ¾″ provide all the necessary material. As shown in Figure 3 a ¼″ dowel is fitted into the center of the face surface of one of the blocks as shown in *B*, projecting ⅛″ as shown in *C*. The purpose of this projecting dowel being to force the stem of the stopcock loose when placed against it in the jaws of a vice, *X* and

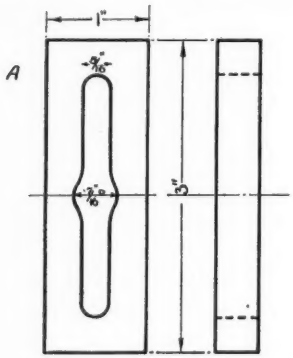


FIGURE 2

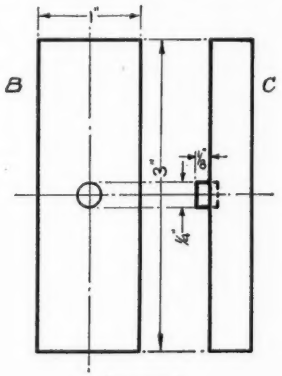
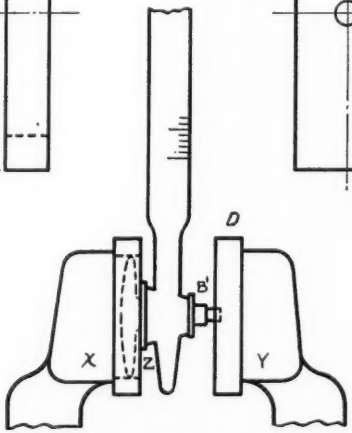


FIGURE 3

FIGURE 1



Y, as shown in Figure 1, it should be cut down as the case demands to fit the opening in the buret as shown at *B'*. In the second block a slot or key way should be cut through, sufficiently large to insert the handle of the stopcock, care being taken to have the inner edge of the aperture fit against the opening of the buret as shown at *Z*. A good method is to bore several holes of the dimensions as shown in Figure 2. The blocks thus formed are placed on either side of the "frozen stopcock" and the ensemble placed between the jaws of a vice where pressure can be applied evenly and slowly, with the result that, in all but the most extreme cases, the stopcock can be removed without breaking.

A SYSTEMATIC ANALYSIS OF THE ANIONS. I

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Herewith is presented a systematic scheme for the qualitative separation and identification of the anions. The reagents used are inexpensive and the procedure is simple enough to be used by freshman and sophomore classes. By exercising proper care, the tests are sufficiently accurate to detect one or two milligrams of any of the twenty-three more common inorganic anions in ten milliliters of solution in the presence of as much as 500 milligrams of another anion.

. . . . . .

PART I

There is as yet no generally accepted system for the qualitative separation and identification of the anions, such as exists in the case of the positive ions. In the majority of qualitative procedures indication of the presence or absence of the more common anions is sought by a series of tests carried out on separate portions of the material under examination. Undoubtedly this method is useful in cases where there is some previous knowledge of the source of the material and it needs to be examined for only a few ions. However, in cases where the composition is entirely unknown, and especially when the amount of material available for analysis is small, it would be desirable to have at hand a more systematic procedure by which tests for a large number of ions could be carried out on one rather small portion. A number of attempts have been made to systematize the analysis of the anions.

One of the most complete of these procedures is that of A. A. Noyes (*1*). Others have been devised by George W. Sears (*2*), G. L. Coyle (*3*), Milobendeskii (*4*), Curtman & Hart (*5*), Curtman & Plechner (*6*), Karaglanov & Dimitrov (*7*), and Fernandez & Gatti (*8*). None of these, however, have proved satisfactory.

The purpose of these procedures has been to develop a systematic analysis which should make use of inexpensive reagents, and which should be simple enough to be used by large freshman or sophomore classes, and yet sufficiently accurate to detect one or two milligrams of any of the more common inorganic anions in ten milliliters of solution in the presence of as much as 500 milligrams of any other anion.

General Discussion

The anions which are included in the system of analysis are the following:

* From a thesis submitted by Miss Alice D. Duschak to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Borate	Ferricyanide	Perchlorate
Bromate	Ferrocyanide	Phosphate
Bromide	Fluoride	Sulfate
Carbonate	Hypochlorite	Sulfide
Chlorate	Iodate	Sulfite
Chloride	Iodide	Thiocyanate
Chromate	Nitrate	Thiosulfate
Cyanide	Nitrite	

In the procedure for the detection of the anions as many ions as possible have been separated into groups based on the solubilities of their calcium, barium, cadmium, and silver salts, as follows:

Group I Ions whose calcium salts are insoluble in neutral solutions.

Group II Ions whose calcium salts are soluble, but whose barium salts are insoluble in neutral solutions containing 20% of acetone by volume.

Group III Ions whose calcium and barium salts are soluble, but whose cadmium salts are insoluble in neutral solutions.

Group IV Ions whose calcium, barium, and cadmium salts are soluble but whose silver salts are insoluble in solutions slightly acid with HNO_3.

Group V Ions whose salts are practically all soluble.

Since some of the ions form difficultly soluble salts with more than one of the group reagents, these ions may be found in more than one group. For this reason the separation of the anions into groups is not so definite and clean-cut as the separation of the cations. In the outline for division into groups (Table I), formulas enclosed in parentheses indicate precipitates which are formed only in solutions containing high concentrations of the anions concerned, and which, therefore, may not always be found in the groups under which they are shown. Discussions of the individual cases are included in the procedures for the respective groups.

In carrying out this system of analysis it is assumed that the anions are present in solution in the form of soluble salts. In the analysis of an insoluble substance the solution may be prepared by any of the standard methods. Since the separation into groups depends on the precipitation of substances insoluble in water but in many cases soluble in acids, it is essential that the solution at the beginning of the analysis be neutral or slightly basic. If it is acid, it should be neutralized by a very slight excess of sodium carbonate, any precipitate formed being filtered off and rejected. If strongly basic, it should be nearly neutralized with acetic acid.

In precipitating the first three groups the acetates of calcium, barium, and cadmium are used as precipitating agents for two reasons:

1. The acetate ion has neither an oxidizing nor a reducing action, and forms no insoluble salts with the ions used as group reagents, and, therefore, does not destroy any of the anions or interfere with the separation of any of the groups.

2. Solutions of the acetates of calcium, barium, and cadmium are slightly basic, due to hydrolysis, while the corresponding salts of the strong acids are slightly acidic. Since these group separations depend on the insolubility of the salts in neutral solutions, the acidity produced by hydrolysis in solutions of salts other than acetates may be sufficient to prevent complete precipitation.

The general precautions to be observed in carrying out the analysis may be listed briefly as follows:

1. Keep solutions cool and neutral or slightly basic until after Group IV is precipitated.

2. Keep volumes as small as possible by using the smallest volume of each precipitating agent that will give complete precipitation and by rejecting all but one or two small washings in each case.

3. Some of the precipitates are very finely divided and have a tendency to pass through the filter paper. In cases where even a fine-grained paper will not retain the precipitate, filter paper pulp is found a very useful aid to filtration.

TABLE I

Division into Groups

Neutral solution containing all anions. Add $Ca(CH_3CO_2)_2$

Precipitate	*Filtrate:* Add $Ba(CH_3CO_2)_2$ and acetone				
$CaCO_3$ CaF_2 $CaHPO_4$ $[CaSO_3]$ $[Ca_2Fe(CN)_6]$ $[Ca(IO_3)_2]$ $[CaSO_4]$ $[Ca(BO_2)_2]$	*Precipitate*	*Filtrate:* Add $Cd(CH_3CO_2)_2$			
	$BaSO_4$ $BaSO_3$ $BaCrO_4$ $Ba(IO_3)_2$ $[Ba(BrO_3)_2]$ $[BaS_2O_3]$ $[Ba_2Fe(CN)_6]$	*Precipitate*	*Filtrate.* Add $NiNO_3$		
		$Cd_2Fe(CN)_6$ $Cd_3[Fe(CN)_6]_2$ CdS $[Cd(CN)_2]$ $[Cd(BO_2)_2]$	*Precipitate*	*Filtrate:* Add $AgNO_3$ and HNO_3	
			$Ni(CN)_2$	*Precipitate*	*Filtrate*
				$AgCl$ $AgBr$ AgI $AgCNS$ $Ag_2S_2O_3$ $\rightarrow Ag_2S$	ClO^- ClO_3^- ClO_4^- BrO_3^- $[IO_3^-]$ NO_3^- NO_2^- $[BO_2^-]$

PART II

Procedure I. Analysis of Group I

1. Precipitation of the Calcium Salts.—To the neutral or slightly basic solution containing all the anions add a 2 *N* calcium acetate solution until the precipitation is complete. Stir or shake the mixture well and allow it to settle. Filter the mixture, and wash the precipitate thoroughly with hot water.

2. Identification of the Carbonate Ion.*—Dry the group precipitate thoroughly in a drying oven at 110°C. or by heating it carefully in an evaporating dish over a small flame, and transfer it to a small flask equipped with a two-hole stopper carrying a delivery tube connected to two test tubes. Insert in the other opening a glass tube closed by a rubber tube and pinch clamp. The first test tube contains Br_2 water to absorb SO_2, and the second a saturated solution of $Ba(OH)_2$. Add 10 to 15 ml. of 6 *N* acetic acid to the precipitate in the flask, assemble the apparatus quickly, and boil the mixture gently for about a minute. If no precipitate appears in the $Ba(OH)_2$ solution, remove the pinch clamp and attach a drying tube filled with soda lime to the flask. By applying gentle suction to the exit tube from the second test tube aspirate carbon-dioxide-free air through the system at a rate of about two bubbles per second. A white precipitate of $BaCO_3$ in the $Ba(OH)_2$ solution shows the presence of a *carbonate*.**

3. Identification of the Sulfite Ion.—Add 1 or 2 ml. of HCl to the Br_2 solution. Heat the solution to boiling, add a few milliliters of $BaCl_2$ solution, and boil the solution for a few seconds. A white precipitate of $BaSO_4$ shows the presence of a *sulfite* in the unknown solution.

4. Identification of the Phosphate and Fluoride Ions.—Filter the mixture in the flask (Procedure I, 2). To the filtrate add a little cadmium acetate solution to remove any ferrocyanide which may be present. If a precipitate forms, filter the mixture and test the filtrate for a phosphate as follows: Add a slight excess of NH_4OH and then enough HNO_3 to make the solution just acid. Place the solution in a test tube, add a large excess of ammonium molybdate solution, and warm the contents of the test tube by placing the test tube in a beaker of hot water (kept at 70–80°C.). A bright yellow precipitate shows the presence of a *phosphate*.†

Transfer the residue insoluble in acetic acid to a porcelain crucible, dry it carefully, and burn off the filter paper. Mix the ash thoroughly with two or three times its volume of powdered quartz (not artificially prepared SiO_2) and transfer the mixture to a *dry* test tube. Add to it enough concentrated H_2SO_4 to make a thin paste, introducing the acid very carefully so as not to wet the sides of the test tube. Insert in the tube a cork bearing a glass rod with a drop of water on the end. The cork should have a notch cut in one side to let out the vapors. Warm the tube gently over a small flame (not enough to cause evolution of SO_3 fumes). A white precipitate of silicic acid in the drop of water shows the presence of a *fluoride*. This test may be made more sensitive by using a glass rod which has been drawn out and bent into a loop. The loop will hold a thin film of water in which the white precipitate shows up very plainly.

In case no test for a phosphate was obtained above, cool the mixture which has just been tested for a fluoride, dilute it with cold water to 10 or 15 ml. and filter off the quartz. Make the filtrate alkaline with NH_4OH, then just acid with HNO_3, and test for the phosphate ion as directed above.

---

* If Na_2CO_3 has been used in preparing the solution, the test for the carbonate ion may be carried out on a portion of the original unknown solid or solution in the same manner.

** If the Br_2 water becomes decolorized during the passage of the gas it must immediately be replaced by a fresh solution. Otherwise SO_2 passing into the $Ba(OH)_2$ solution will produce a precipitate of $BaSO_3$ which may be mistaken for $BaCO_3$.

† If in the cation analysis arsenic has been found to be present, it must be removed before the test for a phosphate is made, since it gives a yellow precipitate with ammonium molybdate very similar to that given by phosphates. Arsenic is removed by making the solution acid with HCl and passing H_2S into it. The arsenic sulfide is filtered off, and the filtrate is then tested for the phosphate ion, after expulsion of H_2S.

TABLE II

Procedure I. Analysis of Group I

Neutral solution containing all anions. Add $Ca(CH_3CO_2)_2$

Precipitate: $CaCO_3$, ($CaSO_3$), $CaHPO_4$, CaF_2, ($CaSO_4$), [$Ca_2Fe(CN)_6$], [$Ca(IO_3)_2$], [$Ca(Bo_2)_2$]. Dry, add CH_3CO_2H, boil, pass gases through Br_2 water into $Ba(OH)_2$ solution

$Ba(OH)_2$ solution. *White precipitate* $BaCO_3$, shows *Carbonate*	*Br_2 water* Add HCl, $BaCl_2$. White precipitate, $BaSO_4$, shows *Sulfite*	*Mixture in flask.* Filter			
		Residue: CaF_2, [$CaHPO_4$], [$Ca(IO_3)_2$], [$Ca_2Fe(CN)_6$]. Ignite heat with powdered quartz and conc. H_2SO_4. Hold drop of H_2O in vapor		*Filtrate:* Add $Cd(CH_3CO_2)_2$	
				Precipitate: $Cd_2Fe(CN)_6$ Reject	*Filtrate:* Add NH_4OH, HNO_3, $(NH_4)_2MoO_4$. Yellow precipitate shows *Phosphate*
		Drop of H_2O White precipitate, H_4SiO_4, shows *Fluoride*	*Mixture in test tube* Test for *Phosphate*		

Discussion of the Analysis of Group I

In a neutral solution, calcium acetate precipitates the carbonate, phosphate, and fluoride ions almost completely by forming insoluble $CaCO_3$, $CaHPO_4$, and CaF_2. If the solution is alkaline the phosphate precipitate is probably $Ca_3(PO_4)_2$. The sulfite ion will also be precipitated in this group unless the concentration is very low. If high concentrations of the ferrocyanide and iodate ions are present, they will also give precipitates on the addition of calcium acetate, but sufficient amounts will always remain in solution so that tests for these ions will be obtained in their respective groups.

A Group I precipitate which is difficult to filter may be calcium fluoride which is very slimy when freshly precipitated. If such a precipitate is obtained, filtration may be facilitated by adding 1 ml. of Na_2CO_3 solution. A mixture of CaF_2 and $CaCO_3$ is much easier to filter than CaF_2 alone. If Na_2CO_3 is added, the test for a carbonate must be made on a portion of the original unknown.

The group precipitate is dried before treating it with acetic acid because freshly precipitated CaF_2 is somewhat soluble in acetic acid besides being difficult to filter. Drying the precipitate both decreases its solubility and makes it easier to filter.

The Carbonate Ion.—Calcium carbonate reacts with warm acetic acid

to give CO_2 which precipitates $BaCO_3$ from a solution of $Ba(OH)_2$. Any SO_2 is first removed by passing the gas through a solution of Br_2. If the amount of CO_2 evolved is so small that it is not driven over into the $Ba(OH)_2$ solution by boiling the acetic acid solution, it will be carried over when air is drawn through the system. The soda lime bulb is used to absorb the CO_2 from the air which would otherwise give a precipitate of $BaCO_3$. It must be remembered that on boiling the solution the air already in the system will be driven over and may contain enough CO_2 to give a precipitate. For this reason as small a flask as possible should be used. If a small precipitate is obtained a blank may be run using the same size flask and the same volume of solution without any carbonate.

The Sulfite Ion.—$CaSO_3$ reacts with warm acetic acid to form H_2SO_3, which on boiling breaks down completely into H_2O and SO_2. The SO_2 passes over into the solution of Br_2 and is oxidized to sulfuric acid. On adding $BaCl_2$ to the solution which has been acidified with HCl, a precipitate of $BaSO_4$ is obtained.

The Phosphate Ion.—Dried calcium phosphate is not entirely soluble in acetic acid, even on boiling. Usually enough dissolves to give a test in the acetic acid solution. However, in the presence of the fluoride ion a double salt of calcium fluoride and phosphate is formed which is insoluble in acetic acid. In this case the phosphate may all be present in the residue containing the CaF_2 and the test must be made on the mixture left from the fluoride test. The test for the phosphate ion depends on the formation of the yellow precipitate having the formula $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 6H_2O$, on the addition of a large excess of ammonium molybdate to the solution just acid with HNO_3. The arsenate ion if present would give a similar precipitate, and must, therefore, be removed before testing for phosphate. The separation of a small amount of ferrocyanide is made by precipitating cadmium ferrocyanide from the acetic acid solution. The phosphate remains in the solution, since cadmium phosphate is soluble in 6 *N* acetic acid.

If a cation analysis has been made, the presence or absence of the phosphate ion will already have been determined and this test may be omitted.

The Fluoride Ion.—Dried CaF_2 is almost insoluble in acetic acid, but reacts with hot concentrated H_2SO_4, liberating HF. The HF reacts with the powdered quartz (which is almost pure SiO_2) to form SiF_4 which is driven off as a gas and on coming in contact with the drop of water, reacts with it forming a white precipitate of orthosilicic acid (H_4SiO_4) having hydrofluosilicic acid (H_2SiF_6) in solution. It is necessary to use powdered quartz, and not artificially prepared SiO_2, since the latter retains much of the fluorine instead of liberating it as SiF_4. It is absolutely necessary to have the test tube and all the materials perfectly dry, for if any water is present the SiF_4 will be decomposed before it comes into contact with the drop on the end of the glass rod.

PART III

Procedure II. Analysis of Group II

1. Precipitation of the Barium Salts.—To the filtrate from Group I, Procedure I, 1, add a 2 *N* barium acetate solution until no more precipitate is formed, then 1 or 2 ml. more. Then add a volume of acetone equal to $^1/_4$ the volume of the solution, stir the mixture thoroughly, and allow it to stand for ten minutes. Filter the mixture, using a fine-grained filter paper, and wash the precipitate with cold water containing a little $Ba(CH_3CO_2)_2$ and 20% acetone by volume.

2. Identification of the Bromate Ion.—Punch a hole in the bottom of the filter paper containing the barium precipitate, and with a stream of hot water from the wash bottle wash the precipitate back into the beaker in which the precipitation was made. Add a little barium acetate and boil the mixture for a minute or two. Filter the mixture and wash the insoluble residue with hot water. The filtrate should contain all of the bromate and a little of the iodate. It may contain some ferrocyanide or thiosulfate if a high concentration of either ion was present in the original solution. Acidify the filtrate with acetic acid and add a few drops of cadmium acetate. If a precipitate of cadmium ferrocyanide forms add cadmium acetate until the ferrocyanide is all precipitated. Filter, and wash the precipitate. The ferrocyanide ion may be identified at this point by dissolving the precipitate in dilute HCl and adding to the solution a little $FeCl_3$. A dark blue precipitate (see Procedure III, Analysis of Group III) shows the presence of a ferrocyanide.

Pass SO_2 into the filtrate from the cadmium ferrocyanide precipitate (or the hot water solution if no ferrocyanide was found present), or add sulfurous acid until the solution smells strongly of SO_2. Boil the solution until it no longer smells of SO_2 and filter off the $BaSO_4$ precipitated. Transfer the cooled solution to a separatory funnel, add 1 ml. of dilute HNO_3 and 2 ml. of carbon tetrachloride and then ferric nitrate solution until the water layer is colored yellow. Shake the mixture well. A violet color in the CCl_4 layer indicates the presence of an *iodate*. If an iodate is found, reject the CCl_4 layer, transfer the water layer to a beaker, and boil it for one minute to expel iodine, being sure that an excess of ferric nitrate is present. Cool the solution, and return it to the separatory funnel and extract it again with CCl_4 to insure the complete removal of I_2. Add 2 ml. of CCl_4, 2 ml. of HNO_3, and then $KMnO_4$ solution until the water layer is purple. Shake the mixture well. A yellow to orange color in the CCl_4 indicates the presence of a *bromate*.

3. Identification of the Sulfite Ion.—Transfer the residue which was insoluble in hot water to a small flask equipped with a delivery tube dipping into bromine water. Add 10–20 ml. of 2 *N* HCl to the residue, assemble the apparatus quickly, heat the mixture in the flask to boiling and boil it for one minute. Test the Br_2 solution for a sulfate as in the analysis of Group I, Procedure I, 3. A precipitate of $BaSO_4$ shows the presence of a *sulfite* unless a high concentration of a thiosulfate is present, in which case a special test for the sulfite must be made. The sulfite ion may be identified in the presence of a thiosulfate by adding a solution of a strontium salt. Allow the precipitate to settle and filter it off. Test the precipitate for a sulfite and the filtrate for a thiosulfate.

4. Identification of the Sulfate Ion.—A white residue in the flask, Procedure II, 3, insoluble in hot dilute HCl, is usually a sufficient test for the *sulfate* ion. If there is any doubt, its presence may be confirmed by fusing the ignited residue with a mixture of equal parts of sodium and potassium carbonates, extracting the melt with hot water, acidifying the filtrate, and testing for a sulfate with $BaCl_2$.

5. Identification of the Chromate Ion.—The solution in the flask, Procedure II, 4, may contain the iodate and dichromate ions. Pass SO_2 into the solution or add sulfurous acid or sodium bisulfite until the solution smells strongly of SO_2. Boil off all of

the excess SO_2, filter the mixture, and reject the residue of $BaSO_4$. A color change in the solution from yellow or orange to green indicates the presence of a chromate. Make the solution just alkaline with NH_4OH, heat it to boiling, and boil for two or three minutes. A greenish blue precipitate is $Cr(OH)_3$. To confirm the presence of the chromate, filter out the precipitate and dissolve it in dilute HNO_3. Make the solution alkaline with NaOH and add Na_2O_2 in small portions until the chromite is completely oxidized to chromate. Boil the solution to decompose the excess Na_2O_2, add a slight excess of CH_3CO_2H and a few ml. of $AgNO_3$. A brownish red precipitate of Ag_2CrO_4 confirms the presence of a chromate.

6. Identification of the Iodate Ion.—If no test for an iodate was obtained in Procedure II, 2, cool the filtrate from the $Cr(OH)_3$ precipitate, Procedure II, 5, and acidify it with HNO_3. Transfer it to a separatory funnel, and test for an iodate as in Procedure II, 2.

TABLE III

Procedure II. Analysis of Group II

Filtrate from Group I. Add $Ba(CH_3CO_2)_2$ and acetone

Precipitate: $BaSO_4$, $BaSO_3$, $BaCrO_4$, $Ba(IO_3)_2$, $[Ba(BrO_3)_2]$, $[Ba_2Fe(CN)_6]$, (BaS_2O_3) Boil with H_2O and $Ba(CH_3CO_2)_2$

Precipitate: $BaSO_4$, $BaSO_3$, $BaCrO_4$, $Ba(IO_3)_2$, (BaS_2O_3). Boil with HCl, pass gas into Br_2 water

Filtrate: BrO_3^-, (IO_3^-), $(S_2O_3^=)$, $[Fe(CN)_6^{\equiv}]$. Add CH_3CO_2H and $Cd(CH_3CO_2)_2$

Br_2 solution: Add HCl, $BaCl_2$ White precipitate, $BaSO_4$, shows *Sulfite* (or *Thiosulfate*)

Mixture in flask. Filter.

Residue: $BaSO_4$ shows *Sulfate*

Filtrate: IO_3^-, $Cr_2O_7^=$. Add SO_2, green color shows *Chromate*. Add NH_4OH

Precipitate: $Cr(OH)_3$ Add HNO_3, NaOH, Na_2O_2, CH_3CO_2H, $AgNO_3$. Red-brown precipitate Ag_2CrO_4, confirms *Chromate*

Filtrate: I^- Add HNO_3 $Fe(NO_3)_3$, CCl_4. Violet color in CCl_4, I_2, shows *Iodate*

Precipitate: $Cd_2Fe(CN)_6$ Add HCl, $FeCl_3$. Blue precipitate shows *Ferrocyanide*

Filtrate: Add SO_2, HNO_3, $Fe(NO_3)_3$, and CCl_4.

CCl_4 layer. Violet color, I_2, shows *Iodate*

Water layer. Boil, add HNO_3, $KMnO_4$, CCl_4. Yellow color in CCl_4, Br_2 shows *Bromate*

Discussion of the Analysis of Group II

In a neutral solution the sulfite, sulfate, and chromate ions are almost completely precipitated as insoluble barium salts by the addition of barium acetate. The precipitation of barium iodate is less complete, and barium bromate is not precipitated at all unless a high concentration

of bromate ion is present. The solubilities of these two salts are greatly reduced by the addition of acetone. In a neutral solution containing an excess of barium acetate and 20% acetone by volume, barium iodate is almost completely precipitated. The precipitation of barium bromate is still far from complete, but the bromate ion is removed completely enough so that no precipitate of silver bromate is obtained in Group IV, thus insuring the separation of bromide and bromate. It is important to add an excess of barium acetate *before* the acetone is added, otherwise the precipitation of barium iodate and barium bromate is not satisfactory. In the presence of acetone the ferrocyanide ion is partially precipitated as barium ferrocyanide but is easily separated in the analysis of the group. Enough is always left in the solution to give a test in Group III, but it is well to make the test in this group also, since it can be made very easily and may save time in the analysis. Barium thiosulfate may also be precipitated if the concentration of the thiosulfate ion is high, but enough remains in the solution to give a good test in Group IV.

Barium sulfate and barium sulfite form very fine precipitates which have a tendency to pass through the filter paper. Usually this can be prevented by use of a fine-grained paper. If this does not completely retain the precipitate, filter paper pulp may be used.

The Bromate Ion.—Barium bromate is easily soluble in hot water. Barium ferrocyanide if present will also be completely dissolved, but is removed by precipitation with cadmium acetate from a solution slightly acid with acetic acid, in which cadmium iodate is somewhat soluble and therefore not precipitated. If barium thiosulfate has been precipitated it will be partially dissolved, but will not interfere with the test for the bromate. A little barium iodate may dissolve in the hot water, and a test should be made for the iodate ion in this solution, for if not removed it may obscure the test for the bromate ion. The bromate and iodate ions are reduced by an excess of SO_2 to the bromide and iodide, respectively. After boiling off the excess SO_2, the iodide is oxidized by ferric nitrate in the presence of a little HNO_3 to free iodine, which gives a violet color on extraction with carbon tetrachloride. On boiling for a minute in the presence of an excess of ferric nitrate the iodide is all oxidized and driven off as iodine, while the bromide is not oxidized appreciably, on account of the difference in reduction potentials of the two ions. The bromide is then oxidized to free bromine by potassium permanganate and extracted by carbon tetrachloride, giving a yellow or orange color.

The Iodate Ion.—The greater portion of barium iodate, unless the amount is very small, is not dissolved by the hot water, especially in the presence of a little barium acetate. It is dissolved, however, by hot 2 *N* HCl and is subsequently reduced to iodide and identified in the same manner as above, after removing the chromic ion as hydroxide.

The Sulfite Ion.—Barium sulfite is almost insoluble in water, but easily soluble in HCl, forming the unstable H_2SO_3 which decomposes completely on heating, with evolution of SO_2. This test should always be made in this group if the sulfite ion has not been found in Group I. In case barium thiosulfate has precipitated it will also dissolve in HCl, giving SO_2 and thus making the test for the sulfite inconclusive, and a separate test must be made as directed. This depends on the difference in the solubilities of strontium sulfite and thiosulfate. Strontium sulfite is much less soluble and is, therefore, easily precipitated, while the thiosulfate remains in solution.

The Sulfate Ion.—Since $BaSO_4$ is the only barium salt of the group which is insoluble in HCl, a white residue left from the HCl treatment may usually be taken as sufficient evidence of the presence of the sulfate ion. However, $Ba(IO_3)_2$ dissolves rather slowly in HCl, and if a large amount is present, a white residue may be $Ba(IO_3)_2$ and not $BaSO_4$. If there is any doubt, the confirmatory test should be made. A flux of the mixed alkali carbonates is used rather than Na_2CO_3 alone because of its much lower melting point. By this fusion the sulfate ion is obtained in soluble form as the sodium and potassium salts and the barium is converted to the carbonate, which is left as an insoluble residue on extracting the melt with water. The solution is then tested for a sulfate in the regular way.

The Chromate Ion.—$BaCrO_4$ is dissolved in HCl, forming the dichromate ion, which is reduced to the chromic ion by SO_2, as indicated by the color change from orange to green. On adding a very slight excess of NH_4OH and boiling the mixture, $Cr(OH)_3$ is precipitated as a bluish or brownish green gelatinous precipitate. Too large an excess of NH_4OH gives a violet solution, probably due to the formation of a complex ion, which however, is decomposed on boiling, so that the hydroxide is precipitated. When the HNO_3 solution of $Cr(OH)_3$ is made alkaline with NaOH, the chromite ion is formed, which is oxidized to the chromate by Na_2O_2. The formation of Ag_2CrO_4 on adding $AgNO_3$ to the solution acidified with CH_3CO_2H is a sensitive test for a chromate.

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(To be concluded in July issue.)

A NEW METHOD OF SEPARATION AND DETECTION OF THE HALOGEN IONS INVOLVING THE USE OF CHLORAMINE-T

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Fluoride is separated in the usual manner. Iodide is separated from bromide and chloride by treating the neutral solution of their alkali salts with Chloramine-T. Free bromine is liberated from the solution free of fluoride and iodide by adding Chloramine-T and acidifying with hydrochloric acid. A new sample of the neutral fluoride-free solution is treated with bromine water to precipitate iodine. The iodide-free solution is boiled with nitric acid to liberate free bromine from the bromides which is driven off as the boiling is continued. Chloride is then detected in the solution freed from the other halogen ions by means of silver nitrate.

. . . . . .

If to a neutral solution of the alkali halides a solution of Chloramine-T is added, elementary iodine is precipitated. If the precipitated iodine is separated from the rest of the solution by filtration and the filtrate boiled to expel elementary iodine left in the solution, the presence of a bromide can be detected by first adding a few drops of Chloramine-T solution, and then several drops of concentrated hydrochloric acid, which liberates free bromine, indicated by the colorless solution changing to the characteristic color of bromine water. The presence of chloride is detected in a new sample of the original neutral solution, free from fluoride, after expelling bromide and iodide as indicated in the procedure by means of silver nitrate.

There are two interfering factors involved in this method. The first occurs when the iodine is being precipitated by the Chloramine-T. Due to the decomposition of the Chloramine-T, the solution becomes strongly alkaline, with the result that some iodine remains in solution as iodide, hypoiodite, or iodate. However, this effect is greatly minimized by the addition of ammonium acetate, which represses the concentration of hydroxyl ion due to the formation of slightly ionized ammonium hydroxide.

The second also occurs during the precipitation of the iodine, for if too great an excess of Chloramine-T is added, some free iodine is oxidized to iodic acid. This can also be controlled by adding the Chloramine-T to the solution drop by drop, with constant stirring until the mixture becomes black and then adding several additional drops.

Procedure

1. Detection and Separation of Iodides. A 5 cc. portion of the *neutral* or *very faintly alkaline* solution of the alkali halides, which has been freed from fluoride by the ordinary methods, is diluted to 25 cc. and 2–3 grams of ammonium acetate are added. A 5% solution of Chloramine-T

is slowly added, drop by drop, with constant stirring, until a permanent black precipitate is formed. The mixture is filtered and the filtrate is caught in a beaker containing 2 cc. of the Chloramine-T solution. If incomplete precipitation is indicated, by the filtrate turning black, repeat the process with the filtrate, adding Chloramine-T very cautiously. The color of the filtrate should be a pale lemon color, due to some elementary iodine in solution.

The presence of iodide will be immediately shown, just as the first two or three drops of Chloramine-T comes in contact with the solution, by a dark coloration at the point of contact, which may disappear as the solution is stirred. If this effect does not occur, iodide is definitely absent.

The precipitated iodine is filtered off and confirmed by treating it with sodium thiosulfate, in which it immediately dissolves.

2. Detection of Bromides. The filtrate from (1) is diluted to 40 cc. and boiled until the solution becomes *absolutely colorless*. Ten cc. of water are added and the solution reboiled for five minutes. Water may be added if the volume of solution becomes too small. The solution is allowed to cool to 70°, and then several drops of concentrated hydrochloric acid are added. If the solution becomes lemon-colored, bromide is present. If no color change takes place several drops of Chloramine-T should be added and the solution tested with litmus. If it is alkaline it should be acidified with dilute hydrochloric acid, when the color change will take place if bromides are present.

If iodides have been shown to be absent in (1), the presence of bromides can be shown at once by acidifying the solution to which the Chloramine-T has been added, with concentrated hydrochloric acid. If both iodide and bromide are absent the only other anion present is, of course, chloride, which is proved by acidifying a portion of the original fluoride-free solution with nitric acid and adding silver nitrate, thereby causing silver chloride to precipitate.

3. Separation of Iodide and Bromide from Chloride and Detection of the Latter. A new 5 cc. sample of the original *neutral or very faintly alkaline*, fluoride-free solution is diluted to 20 cc.; and bromine water is slowly added with constant stirring, (provided iodides have been shown to be present; otherwise the bromine treatment is unnecessary), until all the iodine has been completely precipitated. The iodine is filtered off and discarded and the filtrate is diluted to 40 cc. Ten cc. of concentrated nitric acid are added and the solution is boiled until it becomes *absolutely colorless*. It is well to continue the boiling for about five minutes after complete decolorization, adding water if necessary. The solution is cooled, a small sample of it is diluted with water and some solution of silver nitrate is added, which shows the presence of chlorides by the formation of the characteristic precipitate of silver chloride. Sometimes due to imperfect

expulsion of iodides and bromides, traces of these anions may be carried over to the chloride test and cause a turbidity. To ascertain the cause of this turbidity, add 5 cc. of concentrated nitric acid to the main part of the solution and boil again for five minutes. Repeat the test for chlorides. If the turbidity reappears only traces of chloride are present.

Notes

1. The volume of solution should not be permitted to fall below 15 cc. during the boiling prior to the test for chlorides, as some chloride may be decomposed into free chlorine which will be expelled with the bromine. Add water if necessary.

2. In the absence of iodides, the presence of bromides is also confirmed, during the boiling prior to the chloride test, by the colorless solution becoming reddish and then colorless again as the boiling is continued.

3. As excess Chloramine-T oxidizes elementary iodine to colorless iodic acid, etc., wherever traces iodides are suspected use a 0.25% solution of the reagent adding it slowly drop by drop.

4. For the benefit of those who may be interested in the reactions of Chloramine-T with the alkali halides, the following equations, kindly furnished by Dr. E. H. Volwiler,* are furnished.

a. Chloramine-T added to an alkaline or a neutral solution of alkali chloride causes no reaction. Chloramine-T added to an acid solution of an alkali chloride causes the following reaction;

$$2CH_3C_6H_4SO_2NaNCl + 2CH_3COOH \longrightarrow CH_3C_6H_4SO_2NCl_2 + CH_3C_6H_4SO_2NH_2 + 2CH_3COONa$$

Dichloramine is precipitated by this reaction.

b. Chloramine-T added to an alkaline or neutral solution of an alkali bromide causes no reaction. Chloramine-T added to an acid solution of an alkali bromide causes the liberation of bromine and the precipitation of toluene sulfon dibromamide.

c. Chloramine-T added to an alkaline solution of an alkali iodide causes no liberation of iodine, if the solution is sufficiently alkaline. Chloramine-T added to a neutral solution of an alkali iodide causes the Chloramine-T to decompose, the solution to become strongly alkaline and to liberate part of the iodine although it is mostly combined as iodide, hypoiodite, or iodate.

Chloramine-T added to an acid solution of an alkali iodide causes the following reaction;

$$CH_3C_6H_4SO_2NaNCl + H_2O \longrightarrow CH_3C_6H_4SO_2NH_2 + NaOCl$$
$$NaOCl + 2HI \longrightarrow I_2 + H_2O + NaCl$$

* Of the Abbott Laboratories, North Chicago, Illinois.

THE INDIANAPOLIS MEETING

Report of the Secretary of the Division of Chemical Education

General

The Division of Chemical Education held a most successful program at the 81st meeting of the American Chemical Society. There were but few deviations from the schedule as announced in the April issue of THIS JOURNAL (Vol. **8**, pp. 251–3).

Three half-day sessions were devoted to the reading of twenty-two papers, most of which will appear in full in the JOURNAL OF CHEMICAL EDUCATION. Attendance figures rarely fell below 150 and reached 300 at the Symposium when five invited speakers discussed the problems of "Coöperation between Industry and Chemical Education."

One hundred eighty members and guests attended the Division luncheon* at the Columbia Club Tuesday noon, at the close of which CHAIRMAN JOHN N. SWAN introduced MOSES GOMBERG, President of the A. C. S.; L. V. REDMAN, President-Elect; H. E. HOWE, Editor of *Industrial and Engineering Chemistry;* NEIL E. GORDON, Editor of the JOURNAL OF CHEMICAL EDUCATION; PAULINE BEERY MACK, Editor of *The Chemistry Leaflet;* RUSSELL WILLSON, President of the Indianapolis School Board; and WM. M. BLANCHARD, Dean and Head of the Chemistry Department of DePauw University. Each speaker paid tribute to the teaching profession and proclaimed his interest and faith in the cause of chemical education.

Thursday, one hundred fifty members of the Division took the all-day trip by bus to Bloomington, as guests of Indiana University and the Limestone Association. After visiting a large limestone quarry and mill in the morning the entire group attended a luncheon at the university and then participated in the exercises dedicating Indiana University's new chemistry building. Those who made the trip voiced their sincere appreciation to DR. R. E. LYONS, head of the department at I. U. for a most memorable day. Further details of the dedication program will be found elsewhere in this issue (see p. 1217).

The meeting and dinner of the editors of the JOURNAL OF CHEMICAL EDUCATION and *The Chemistry Leaflet* was unusually well attended, the following being present:

NEIL E. GORDON, *Editor-in-Chief;* OTTO REINMUTH, *Associate Editor;* PAULINE B. MACK, *Associate Editor;* ROSS A. BAKER, LYMAN C. NEWELL, and WILHELM SEGERBLOM, *Departmental Editors;* G. A. ABBOTT, BEN H. BALL, H. W. BRUBAKER, A. J. CURRIER, B. S. HOPKINS, T. D. KELSEY, T. R. LEIGH (representing A. P. BLACK), R. N. MAXSON, W. F. RUDD, J. N. SWAN, A. P. SY, and G. H. WHITEFORD, *Contributing Editors.*

With the Editor-in-Chief of THIS JOURNAL in the rôle of chairman, there was an informal but brief and business-like discussion of a number of questions relating to editorial policies, types of articles desirable for

* See page 1219 for picture.

publication, sources of illustrative material, etc. Dinner followed the business meeting. A rising vote of thanks was tendered Mr. Buffum as host of the occasion and Dr. Baker was instructed to convey to him the regrets of the editors that he was unable to be present in person.

About fifteen "foreign" students took advantage of the invitation of the Butler University living centers to be housed as guests during the meeting. Two high schools responded to the invitation of the Division to exhibit some of the work of their chemistry classes. These were Shortridge High School and Arsenal Technical Schools, both of Indianapolis.

In order to make available more time for the reading of papers, the Executive Committee held several meetings and transacted most of the routine business which had accumulated.

Minutes of the Meetings of the Executive Committee

Present: J. N. SWAN, *Chairman;* M. V. MCGILL, *Vice-Chairman;* R. A. BAKER, *Secretary;* ROSALIE M. PARR, *Treasurer;* WILHELM SEGERBLOM and B. S. HOPKINS, *Past Chairmen;* and NEIL E. GORDON, *Editor-in-Chief.*

REPORTS OF OFFICERS

1. **Chairman:** The Chairman presented a brief report which dealt chiefly with committee appointments, each of which has been recorded in the JOURNAL OF CHEMICAL EDUCATION. The report was accepted.

2. **Secretary:** The Secretary reported that there are now 476 active members and 710 associate members. Questions upon which the Executive Committee has voted by letter ballot since the mid-winter meeting have been decided as follows. (1) It was voted to commemorate the tenth anniversary of the founding of the Division by a special program at the Buffalo meeting. Accordingly, the Division of History of Chemistry has been invited to join in the symposium on "The History of Chemical Education in America" in honor of Dr. Edgar Fahs Smith, who was instrumental in founding each of the Divisions concerned. A joint committee consisting of L. C. Newell and R. A. Baker was appointed to arrange the special program for the Buffalo meeting. (2) The committee recommends that either the Associate Editor or the Assistant Editor of the JOURNAL OF CHEMICAL EDUCATION be sent to meetings of the A. C. S. (3) It was voted to grant the Committee on Chemical Education by Radio up to $100.00 during the year 1931. (4) It was voted to request B. S. Hopkins to represent the Division of Chemical Education on the program of the Illinois Association of Chemistry Teachers, February 28. The report was approved.

3. **Local Secretary:** The Local Secretary reported that he had invited 102 secondary-school teachers to be the guests of the Division at the luncheon and that he had received about 40 acceptances. He also reported that 15 students were to be housed in fraternity centers at Butler College without charge. He acknowledged his particular debt to Mr. Walter Geisler of Shortridge High School for making the arrangements, and to the Alpha Chi Sigma Committee for taking care of the registration at headquarters. He also reported upon the local program, the trip to Indiana University, and other features. The report was accepted.

4. **Treasurer:** The Treasurer presented a report of monies received and expended since January 1. The report was accepted.

5. **Business Manager:** The Secretary presented a detailed report from the Business Manager, covering the JOURNAL OF CHEMICAL EDUCATION and *The Chemistry Leaflet* and showing an encouraging condition of both. The audit of the Business Manager's report for 1930 was approved and appears elsewhere in this issue (see pp. 1197–9).

6. **Editor-in-Chief:** The Editor-in-Chief presented a progress report, which was accepted.

REPORTS OF COMMITTEES

1. **Naming and Scope of Committees:** WILHELM SEGERBLOM, *Chairman*, reported at length upon six problems which were referred to his committee by the Executive Committee at its mid-winter meeting. [See J. CHEM. EDUC., **8**, 753 (Apr., 1931).] His recommendations were approved as follows:

(*a*) That the problem of a correspondence course for high-school chemistry teachers be referred to the present committee on **Preparation of High-School Chemistry Teachers.**

(*b*) That a committee be appointed by the chairman on **Minimum Standards,** with J. N. SWAN as chairman. (See *Secretary's Note* below.)

(*c*) That the problem of vocational guidance be referred to M. V. MCGILL, who is making a professional study of this phase of education, with a view to forming a committee on **Vocational Guidance.**

(*d*) and (*e*) That it is inexpedient for the Division of Chemical Education to promote at the present time the training of youth of pre-high-school age in chemistry, except in so far as museums are concerned, and that the museums' part of the problem be referred to the committee on **Visual Aids in Chemical Education.**

(*f*) That a committee be appointed by the chairman on **Optimum Size of Chemistry Classes.** (See *Secretary's Note* below.)

Secretary's Note: Preparatory to the study of each new problem, the committee on **Naming and Scope of Committees** conducts an exhaustive survey of the field to determine the advisability of appointing a new committee. When a new committee is indicated, specific recommendations are made with regard to (*a*) the scope of the work, (*b*) the name of the committee, and (*c*) the committee personnel. Finally, after the new committee has been appointed by the chairman of the Division, the C.O.N.S.O.C. prepares a detailed statement covering the preliminary survey for the guidance of the new committee.

2. **Visual Aids in Chemical Education:** M. V. MCGILL, *Chairman*, presented a progress report which was accepted. It was voted to accept his recommendation that two additional members be appointed to this committee.

3. **Chemical Education of the Non-Collegiate Type:** R. E. BOWMAN, *Chairman*, transmitted a progress report by letter, which was accepted. This committee expects to present a formal report at the Buffalo meeting.

4. **Chemical Education by Radio:** ROBERT F. MCCRACKAN, *Chairman*, transmitted the following report which was accepted.

Education by radio continues in the experimental stage with chemistry holding its own as compared with other sciences broadcast. Many of the weaker stations now have excellent educational programs with liberal provision for chemical subjects, and numerous chemists devote much time to the preparation of suitable talks. The chemistry departments of about one-third of the better schools of the nation have had some part in radio programs in recent years, and more than three-fourths of the heads of departments think radio talks on chemistry worthwhile.

The problem of getting chemistry on the programs of the larger stations and chain systems presents many difficulties, and is naturally tied up with the larger problem of general education by radio. Advertisers pay well for all except the most undesirable hours, and most radio audiences seek entertainment, rather than education, when they tune in. The Federal Radio Commission has done its best to give us as many stations as can be operated without interference, and to allow as much time and power as pos-

sible, but they cannot at present relieve matters. Speakers are encouraged to talk very fast to save time, and to put subject matter on the plane of the thirteen-year-old to hold the audience.

Interest the past year in education by radio has been very gratifying. For the first time in the history of American education the leaders in educational broadcasting gathered last June at The Ohio State University for a ten-day Institute of Radio Education. Forty-nine papers were read and printed. At the Milwaukee meeting in December of the National Council of State Superintendents and Commissioners of Education with the United States Office of Education seven papers dealing with education by radio were read. Your committee is taking keen interest in studying these fifty-six papers and in watching the progress of events.

With television in the offing promising visual aid to the ear, and with scientists hinting that hitherto unused wave lengths may be made available for radio purposes, while inventors are working to give us synchronized and super-powered stations, and with an awakening sense of duty in our lawmakers to reserve a reasonable time on programs for educational subjects, we think we have reason to be optimistic.

5. **Chemistry Libraries:** RUFUS D. REED, *Chairman*, presented a progress report by letter, which was accepted.

6. **Correlation of High-School and College Chemistry:** NEIL E. GORDON, *Chairman*, presented a progress report, which was accepted.

7. **Labels:** JOHN M. MICHENER, *Chairman*, presented by letter the following report, which was accepted.

The committee has received some criticisms of the list which was published as a part of our preliminary report. Some of these suggestions have been referred to E. J. CRANE of the committee on **Nomenclature.** As soon as his reply is received we shall make up a final list and then submit it to the two companies which desire to publish new editions of label books soon.

The reprints of the preliminary report have been sent out to all the laboratory supply companies, also to all teachers of chemistry in high schools that are listed in the directories given in each issue of the JOURNAL OF CHEMICAL EDUCATION. The Division Secretary mailed copies directly to all members of the Senate.

8. **Minimum Equipment for High-School Chemistry:** J. H. JENSEN, *Chairman*, presented a progress report by letter, which was accepted. This committee is now compiling returns from its recent questionnaire and expects to have definite recommendations concerning the list of chemicals before the close of the school year. The revised list will be submitted to the Division for consideration in the near future.

9. **Preparation of High-School Chemistry Teachers:** In the absence of the chairman, a member of the committee, HENRIETTA HAYDEN, presented the following report, which was accepted.

The fourth report of the Committee was presented as a part of the Symposium on "The Qualifications of Chemistry Teachers," at the Cincinnati meeting of the American Chemical Society. It contains a résumé of the previous work of the Committee, and suggestions for improving the general situation. Two hundred copies of a reprint of this report [J. CHEM. EDUC., **8,** 102–6 (Jan., 1931)] were secured and sent to responsible individuals distributed approximately as follows: secretaries of local sections of A. C. S. (30), state directors of public instruction (48), presidents of state teachers' colleges (Pa.) (11), officials of accrediting agencies (13), other officials (5).

The following letter was addressed to secretaries of Local Sections of the A. C. S.:

Enclosed herewith is a copy of the report of the Committee on Preparation of High-School Chemistry Teachers, which was presented at the September meeting of the American Chemical Society at Cincinnati. This report was a part of the Symposium on "The Qualifications of Chemistry Teachers." The committee plans also to send copies of the report to each of the accrediting agencies and to the Director of Public Instruction of each state.

The Division of Chemical Education of the American Chemical Society voted at the Cincinnati meeting, to give special emphasis to the work of this committee. We are therefore asking you to bring this report to the attention of the members of your section who may be interested in the problem of the preparation of high-school teachers of chemistry and other sciences. There are, no doubt, several such members in each local section. Please urge them to give careful consideration to the report and if they are in sympathy with its findings, request them to communicate their approval of the report to the Director of Public Instruction in their state, who will also receive a copy of the report.

The following letter was addressed to Directors of State Departments of Public Instruction:

Enclosed herewith is a report of the Committee on Preparation of High-School Chemistry Teachers. This report was a part of the Symposium on "Qualifications of Chemistry Teachers" held at the September meeting of the American Chemical Society at Cincinnati, Ohio. The preparation of the high-school science teacher is a problem that deserves very careful study, and this committee has endeavored to make a clear unbiased analysis of the problem.

The Division of Chemical Education of the American Chemical Society voted at the September meeting to give special emphasis to the work of this committee. We are therefore sending copies of the report to the secretaries of the local sections of the American Chemical Society (about 80) as well as to the accrediting agencies and to the state departments of Public Instruction.

It is our hope that the report will receive your serious consideration and that it may help in improving the status of secondary science teaching throughout the country.

At the present writing, several replies of an encouraging nature have been received. The facts are now in the hands of the officials who have the authority to formulate the policies and regulations pertaining to the certification of chemistry teachers. The Committee feels that it has done about all that can be done along these lines. Whether or not any improvement is to be accomplished will depend, in large measure, upon the endorsement and "backing" of the secretaries of the local sections of the American Chemical Society. Their influence and encouragement are most urgently needed. The method of procedure is indicated in the letter included above.

10. **Teacher Exchange:** B. S. HOPKINS, *Chairman*, presented a progress report which was accepted.

11. **Teaching Load:** J. E. MILLS, *Chairman*, presented by letter a progress report which was accepted.

12. **Women's Club Study Course:** HARRISON HALE, *Chairman*, presented by letter the following report which was approved.

Your committee on the Women's Club Study Course wishes to report that it has done all in its power during the past year to secure the adoption of this course by women's clubs. These efforts have been to some extent successful, but for an unknown reason the clubs taking the course have been only in Arkansas and in the neighboring states. Appreciation of the ever-present help of The Chemical Foundation is expressed. The offer of the Women's Service Committee, A. C. S., to assist in this work is highly appreciated. This work will be discussed at the women's luncheon at Indianapolis, April 1. The help given by this group of women will be of the greatest value. Most women's clubs begin a course of study in the fall, the subject for this course having been chosen during the spring. Hence, this is the most effective time to have this matter brought to the attention of the clubs concerned. Your Committee will greatly appreciate aid from any member of this Division which can be given toward its efforts to secure on the part of this group of influential women a recognition of the fundamental importance of chemistry in the life of America.

13. **Special Committee on Journal Files:** J. N. SWAN, *Chairman*, reported that he had reviewed twenty-one filing cases of accumulated correspondence relative to the JOURNAL OF CHEMICAL EDUCATION and had succeeded in reducing it to about one-twentieth of its original volume. He found interesting data covering the history of the Division and as a result of his survey made several significant suggestions regarding future policies of the Division.

NEW BUSINESS

1. The tentative program for the Buffalo meeting was approved. [See J. CHEM. EDUC., **8**, 991 (May, 1931) and pp. 1215–6 of this issue.]

2. It was voted to approve the selection of HOYT C. GRAHAM, of State Teachers' College, Silver City, N. M., as a member of the Senate of Chemical Education.

3. It was voted to direct the chairman to appoint an auditing committee of two members to audit the books of the Division or to select some agent to do so.

4. It was voted that the subscription lists of the JOURNAL OF CHEMICAL EDUCATION and *The Chemistry Leaflet* should not be made available to advertisers.

5. A special committee consisting of M. V. MCGILL and the Secretary was appointed to select the best high-school exhibit at the Indianapolis meeting. (NOTE: The prize of $10.00 has been awarded the Arsenal Technical Schools of Indianapolis.)

6. The proposed contract for the publication of THIS JOURNAL and the *Leaflet* was approved as follows:

(*a*) The Chemical Foundation is to continue the entire business management of the JOURNAL OF CHEMICAL EDUCATION and *The Chemistry Leaflet* until June 1, 1932.

(*b*) The editorial policy is to be in the hands of the Division exclusively.

(*c*) The JOURNAL OF CHEMICAL EDUCATION is to be published twelve times a year and the *Leaflet* at least thirty-four times a year.

(*d*) All revenues from advertising, subscription, etc., are to be used to defray the cost of publishing the JOURNAL and *Leaflet*.

(*e*) There shall be no deficit for the Division in connection with the JOURNAL or *Leaflet* at any time during the period of the agreement.

7. The Secretary was instructed to write all Local Sections of the A. C. S. and all Associations of Science Teachers not now represented in the Senate of Chemical Education, describing the organization and functions of the Senate as well as the obligations of the groups represented therein, and asking if they would be interested in such representation. Geographical overlapping is not considered serious.

Appropriations for committee work were approved as follows:

(*a*) Naming and Scope of Committees—$25.00; (*b*) Labels—$10.00; (*c*) Minimum Equipment—$15.00.

Meeting of the Senate of Chemical Education

Present: Ex Officiis—JOHN N. SWAN, *Chairman*, M. V. MCGILL, R. A. BAKER. *Alabama*—JOHN R. SAMPEY, *Arkansas*—HARRISON HALE, *Colorado*—G. H. WHITEFORD, *Connecticut*—C. R. HOOVER (Proxy for G. A. HILL), *Delaware*—A. N. ZECHIEL, *District of Columbia*—GEO. L. COYLE, *Florida*—TOWNES R. LEIGH (Proxy for V. T. JACKSON), *Illinois*—R. E. GREENFIELD, *Illinois*—JOHN C. NESSLER, *Indiana*—FRANK B. WADE, M. G. MELLON, *Kansas*—JOHN M. MICHENER, *Kentucky*—MARIE BORRIES, J. S. PIERCE, *Maryland*—N. E. GORDON, E. EMMET REID, *Michigan*—O. E. MADISON, *Missouri*—CHAS. W. CUNO, L. MCMASTER, *Nebraska*—ROYCE N. LEROY (Proxy for B. C. HENDRICKS), *New Hampshire*—WILHELM SEGERBLOM, *North Dakota*—G. A. ABBOTT, *Ohio*—ROY I. GRADY (Proxy for W. H. CHAPIN), W. C. GANGLOFF, *Oklahoma*—O. M. SMITH, *Rhode Island*—N. W. RAKESTRAW, *West Virginia*—FRIEND E. CLARK

The following committee members were present by invitation: ROBERT F. MCCRACKAN, HENRIETTA HAYDEN, AIDA M. DOYLE.

REPORT OF SECRETARY

The Secretary reported upon the Senate letter ballot of March 13, having distributed in mimeographed form the replies received to date.

COMMITTEE REPORTS

Mimeographed copies of reports were distributed and, in the absence of committee members, read by the Secretary. (See under Executive Committee Minutes.) The following committees were represented by either their respective chairman or committee members: (1) Naming and Scope; (2) Correlation; (3) Labels; (4) Preparation of High-School Teachers; (5) Radio; (6) Visual Education; (7) Women's Club. These reports aroused spirited discussion and many helpful suggestions were received.

NEW BUSINESS

The Senate voted to refer to the committee on **Naming and Scope of Committees** the question of appointing a committee to study the Chemistry Requirements in Pre-professional Courses.

The Senate voted to invite members of standing committees to attend its meetings.

Business Meeting of the Division

5.00 P.M. April 1 J. N. SWAN, *presiding*

1. The Secretary described the tentative plans for the Buffalo meeting.
2. It was the sense of the meeting that the value of the Division program had been considerably increased by adhering strictly to the time schedule.
3. The Editor-in-Chief was requested to publish in color the periodic chart which accompanied the paper read as #20 by R. H. LEROY.
4. It was voted to express the appreciation and thanks of the Division to (*a*) the Indiana Section of the A. C. S., and (*b*) the *Local Secretary*, JOHN R. KUEBLER.

Adjourned—5.30 P.M.

R. A. BAKER, *Secretary*

UNITED STATES CIVIL-SERVICE EXAMINATION FOR JUNIOR SUGAR TECHNOLOGIST

The United States Civil-Service Commission announces an open competitive examination for the position of junior sugar technologist. Applications must be on file with the U. S. Civil-Service Commission at Washington, D. C., not later than June 9, 1931. The examination is to fill vacancies in the Bureau of Chemistry and Soils, Department of Agriculture, for duty in Washington, D. C., or in the field. The entrance salary is $2000 a year.

Competitors will be rated on general chemistry, elementary physics, and mathematics, on practical questions on sugar technology, and on their education, training, and experience.

Except in the case of senior students, who may be examined with the provision that they may not enter on duty until graduated, applicants must have been graduated from a college or university of recognized standing with the completion of at least 118 credit hours, such a course to have included the fundamentals of chemistry, mathematics, and engineering or physics. Two years of suitable experience may be substituted for two years of the educational requirement.

Full information may be obtained from the Secretary of the United States Civil-Service Board of Examiners at the post office or customhouse in any city or from the United States Civil-Service Commission, Washington, D. C.

Discovery of Wave Motion in Positive Particles of Hydrogen. Dr. A. J. Dempster, University of Chicago physicist, whose discovery of wave motion in positive particles of hydrogen has been hailed by prominent physicists as the most important in years, was led to his achievement by a "leaky" magnetic field which was designed to keep out of the picture the very particles in which the wave motion was found. This discovery is said to open the way for the proof of the hypothesis that all matter is substantially the same, and that the various elements are merely matter under different conditions of motion. Dr. Dempster's discovery was made by deflecting hydrogen atoms off a crystal in a vacuum, upon a photographic plate, at a speed 1,000,000 times that of ordinary light.—*Chi Beta Phi Record*

JOURNAL OF CHEMICAL EDUCATION

STATEMENT OF CASH RECEIPTS AND DISBURSEMENTS

FOR PERIOD NOVEMBER 21, 1927, TO DECEMBER 31, 1930

	Nov. 21/27 to Dec. 31/29	Year 1930	Total
Balance taken over Nov. 21, 1927, from Erle M. Billings, business manager, Educational Division, American Chemical Society	$1,013.41	.....	$1,013.41
Receipts			
Contributions from The Chemical Foundation, Inc.	$64,200.00	$46,000.00	$110,200.00
Subscriptions	37,342.29	19,467.60	56,809.89
Advertising	17,879.48	10,157.37	28,036.85
Reprints	2,172.59	1,959.84	4,132.43
Services Department—Net	183.46	(*10.20*)	173.26
	$121,777.82	$77,574.61	$199,352.43
Total Receipts	$122,791.23	$77,574.61	$200,365.84
Disbursements			
Journal Cost:			
Printing Journal	$76,746.93	$59,023.48	$135,770.41
Editorial Expense:			
Salaries	$17,194.93	$10,953.24	$28,148.17
Abstractors' Fees	801.60	664.00	1,465.60
Traveling Expense	2,605.51	440.40	3,045.91
Stationery and Office Supplies	906.01	457.42	1,363.43
Miscellaneous	1,198.78	470.86	1,669.64
	$22,706.83	$12,985.92	$35,692.75
Total Journal Cost	$99,453.76	$72,009.40	$171,463.16
Sundry Expense Incurred prior to Dec. 1, 1927	$8,823.14	$.....	$8,823.14
Circulation Expenses—Miscellaneous Printing, Postage, Advertising, etc.	7,113.35	1,862.60	8,975.95
Furniture and Fixtures—Desks, Typewriters, Files, etc.	778.15	167.60	945.75
Printing Reprints	3,217.95	2,468.43	5,686.38
Telephone and Telegraph	297.51	239.55	537.06
Auditing	105.00	125.00	230.00
(*Carried Forward*)	$119,788.86	$76,872.58	$196,661.44

	Nov. 21/27 to Dec. 31/29	Year 1930	Total
(Brought Forward)	$119,788.86	$76,872.58	$196,661.44
Stationery and Office Supplies	476.31	69.50	545.81
Postage	1,094.18	476.40	1,570.58
Insurance on Life of Dr. Gordon	563.50	*(121.00)*	442.50
Miscellaneous	435.98	194.17	630.15
Total Disbursements	$122,358.83	$77,491.65	$199,850.48

Summary

Total Receipts	$122,791.23	$77,574.61	$200,365.84
Total Disbursements	122,358.83	77,491.65	199,850.48
Balance in Bank and on Hand, December 31, 1929	$ 432.40		
Excess of Receipts over Disbursements for Year 1930		$ 82.96	
Balance in Bank and on Hand, December 31, 1930			$ 515.36

We hereby certify that the above Statement of Cash Receipts and Disbursements is in accordance with the books of the JOURNAL OF CHEMICAL EDUCATION for the period November 21, 1927, to December 31, 1930.

(Signed) PASLEY AND CONROY,
Certified Public Accountants

Dated March 18, 1931

Approved, March 30:

J. N. SWAN, *Chairman*
MARTIN V. MCGILL, *Vice-Chairman*
R. A. BAKER, *Secretary*
R. M. PARR, *Treasurer*
WILHELM SEGERBLOM, *Past Chairman*
WM. MCPHERSON, *Past Chairman*
NEIL E. GORDON, *Editor-in-Chief*

Industrial Interest Shown in Maizolith, New Cornstalk Material. So much public interest has been aroused in the substance, maizolith, developed by C. E. Hartford, Jr., at the U. S. Bureau of Standards, that the Bureau has had to take up the work again in order to supply the demands for samples.

The story of maizolith concerns a senior student at the Iowa State College, and his laboratory thesis. Young Mr. Hartford, who was working for a degree at Iowa State, discovered that if cornstalk pulp is put through certain mechanical operations and then combined with water, it will form a tough jelly. When this jelly dries it is tough and horny and much like hard rubber.

The Bureau of Standards asked Mr. Hartford to come on the government payroll and work on his cornstalk rubber. Mr. Hartford came to Washington, completed his work, wrote a paper on it, and resigned. The Bureau considered the matter closed and the work finished, but suddenly there developed such a continuous public demand for samples of maizolith, that a man had to be put back on the cornstalk rubber detail.

"The project is again active," says the Bureau.—*Science Service*

THE CHEMISTRY LEAFLET

STATEMENT OF CASH RECEIPTS AND DISBURSEMENTS

FOR PERIOD OCTOBER 19, 1929, TO DECEMBER 31, 1930

Receipts			
Contributions from The Chemical Foundation, Inc.			$15,400.00
Subscriptions			18,152.95
Advertising			410.40
Total Receipts			$33,963.35
Disbursements			
Journal Costs:			
Printing and Mailing Journal		$27,611.32	
Editorial Expense:			
Editor's Salary	$2,000.00		
Traveling Expenses	260.28		
Clerical and Office Expenses	863.19		
News Bulletin, Periodicals, etc.	211.63		
Miscellaneous	263.71	3,598.81	
		$31,210.13	
Other Expenses:			
Circulation Expenses — Miscellaneous Printing, etc.	$493.85		
Review Contest Prizes	135.00		
Furniture and Fixtures	52.25		
Stationery and Office Expense	357.00		
Postage	404.50		
Miscellaneous	21.42	1,464.02	
Total Disbursements			32,674.15
Balance in Bank at December 31, 1930			$1,289.20

We hereby certify that the above Statement of Cash Receipts and Disbursements is in accordance with the books of *The Chemistry Leaflet* for the period October 19, 1929, to December 31, 1930.

(Signed) PALSEY AND CONROY,
Certified Public Accountants

Dated March 24, 1931

Approved, March 30:

J. N. SWAN, *Chairman*
MARTIN V. MCGILL, *Vice-Chairman*
R. A. BAKER, *Secretary*
R. M. PARR, *Treasurer*
WILHELM SEGERBLOM, *Past Chairman*
WM. MCPHERSON, *Past Chairman*
NEIL E. GORDON, *Editor-in-Chief*

It takes a big man to be really humble and to display becoming modesty.—ROBERT MILLIKAN

Abstracts

APPARATUS, LABORATORY PRACTICE, AND DEMONSTRATIONS

The Determination of Metals with 8-Hydroxyquinoline. *Syn. Org. Chem.*, **4,** No. 3 (Feb., 1931).—The phenolic hydrogen of this compound is readily replaced by metals, forming in many cases insoluble precipitates. Valuable separations can be accomplished using this reagent and varying the pH of the solution. The reagent is an excellent precipitant for aluminum. H. H. K.

KEEPING UP WITH CHEMISTRY

The Diamond Mines of South Africa. F. L. GARRISON. *J. Franklin Inst.*, **211,** 197–224 (Feb., 1931).—A history and description of the diamond and its mining dating from 1867, with fifteen photographic illustrations. The following mines are discussed: Consolidated Diamond Mines, Ltd.; Old Kimberley; Namaqua; Premier and Wesselton. Climate, health, and disease of the natives, problems of miscegenation, social status of the whites, problems of government, problems of business, prestige of the British and Americans among the natives and reasons for the same, are discussed in an entertaining and instructive fashion. J. H. G.

A Survey of the World Position of Nitrogen. (I). G. C. RILEY AND H. G. BOTT. *Chem. Age*, **24,** 161–2 (Feb. 21, 1931); **(II),** *ibid.*, **24,** 188–9 (Feb. 28, 1931).—In 1929, 3,100,000 tons of fixed nitrogen compounds were prepared synthetically, a large increase over the amount made in 1928, 2,600,000 tons. It has been calculated that the known nitrate deposits are capable of supplying 3,000,000 tons of nitrate a year for 70 years. The writer predicts that in the future ammonia will be a by-product, not of the gas industry, but of a great synthetic organic chemistry industry. E. R. W.

Phosphates and Superphosphates: A World Survey. A. N. GRAY. *Chem. Age*, **24,** 90–1 (Jan. 31, 1931).—Since the Great War finely ground phosphate rock as a fertilizer has increased although in quantity used it is still far behind the more soluble superphosphate of which about 15,000,000 tons were used in 1929. E. R. W.

History Repeats Itself: Corn Sirup 1907—Corn Sugar 1930. EDITORIAL. *Am. J. Pharm.*, **103,** 57–9 (Feb., 1931).—In 1907 the U. S. Board of Food and Drug Inspection came to the conclusion that corn sirup was not a satisfactory synonym for glucose. The Corn Products Co. protested this decision and backed up their protest with a large number of opinions of eminent chemists. The U. S. Board also obtained opinions of some 58 chemists out of which number 55 approved the proposed ruling of the Board that corn syrup was not a proper name for glucose; but this ruling was overruled in 1908 by the Secretary of Treasury, Secretary of Agriculture, and Secretary of Commerce and Labor. Now in 1925 there was introduced into the House and Senate of the U. S. a bill providing for the amendment of the Food and Drug Act so that the presence of dextrose (corn sugar), which is now available in a pure white, crystalline form, would not require notification of its presence in foods as distinguished from sucrose (cane sugar). The legislation failed; but Secretary Hyde of the Dept. of Agriculture recently issued the following ruling on the status of corn sugar: "Corn sugar (dextrose) when sold in packages must be labeled as such; when sold in bulk must be declared as such; but the use of pure refined corn sugar as an ingredient in the packing, preparation, or processing of any article of food in which sugars are a recognized element need not be declared upon the label of any such product. Nothing in this ruling shall be construed to permit adulteration or imitation of any natural product, such as honey or other ingredient." Food officials regret that Secretary Hyde used his power to give to the proponents of the undeclared use of corn sugar that which could not be obtained by legislative enactment. G. O.

Cascara. T. J. STARKES AND A. R. WILCOX. *Am. J. Pharm.*, **103,** 73–97 (Feb., 1931).—For the last five years the cascara tree has been under observation by the faculty and senior students at the Oregon State College. It has an interesting history and is supposed to be identical with "Shittim or Chittim" wood used in the Ark of the Covenant and for dowel pins in the construction of Solomon's temple. It was discovered near the Colombia River by the Lewis and Clark Expedition in 1805. Much confusion has resulted because of the many common names applied to the tree. The cascara is a deciduous tree. This is the first of a series of articles which will appear in the *Am. J. Pharm.*, this one describing the species, distribution, growth, and medicinal value. G. O.

The Manufacture and Uses of Edible Gelatin. T. B. DOWNEY. *Hexagon*, **21**, 70–5 (Nov., 1930). H. H. K.

Tantalum Carbide, A New Cutting Metal. ANON. *Met. & Mining Markets*, **2**, 6 (Mar. 5, 1931).—Tantalum carbide, recently placed on the market under the name Ramet, closely approaches diamond in hardness, the commercial grade having a Rockwell hardness of 88.5 to 90.5 in the no load "C" scale. Ramet is produced from powdered tantalum metal, which is converted into carbide, and then ground in a ball mill where nickel is added as a binder. It cuts such "unmachinable" materials as tempered high-speed steel or 15 per cent manganese steel. It has an ultimate tensile strength of 250,000 to 300,000 lbs. per sq. in. and a melting point of about 8000°F. G. W. S.

Ramet. See **Tantalum Carbide, A New Cutting Metal** immediately above.

Wrought Iron by New Process Promises Much for the Industry. C. H. VIVIAN. *Compressed Air Mag.*, **36**, 3426–32 (Mar., 1931).—The opening of a new $12,000,000 plant near Pittsburgh, Penna., for the manufacture of wrought iron on a large scale by a new mechanical process marks an epoch in the age-old history of wrought iron. Wrought iron is practically pure iron with which has been mixed about 3% by weight of an iron silicate. While it is not as strong as steel it has some advantages, namely its resistance to corrosion and its ability to withstand shock and vibration. In some ways it is more easily worked than steel. Steel has largely replaced wrought iron for many purposes largely because it may be produced by mechanical means in large amounts, while up to the present time wrought iron required much hand labor. By this new process, which is described in some detail, wrought iron promises to regain its former position of importance in industry. E. R. W.

Zinc, Cadmium, and Mercury. See this title, page 1203.

Vulcanization of Rubber. See this title, page 1203.

Determination of the Molecular Weight of Insulin. T. SVEDBERG. *Nature*, **127**, 438–9 (Mar. 21, 1931).—The Svedberg, of the Laboratory of Physical Chemistry, University of Upsala, was given 0.25 g. of crystalline insulin from Johns Hopkins University and with this sample made a fairly complete study of the molecular weight by sedimentation methods. The results gave a mean value of 35,100, which is very close to that of egg albumin protein. This fact, coupled with other determinations, make it very improbable that the synthesis of insulin will ever become possible. F. B. D.

Under Invisible Light. J. W. STURMER. *Am. J. Pharm.*, **103**, 62–73 (Feb., 1931).—Another Popular Science Lecture given at the Philadelphia Coll. of Pharm. and Science. It is customary to associate light with visibility; but this is because humans are responsive to certain light waves within a certain span of vibration frequencies. Invisible light or ultra-violet light is radiant energy in wave lengths too short and frequencies too high for our eyes. Even our ordinary units of measurement are impracticable for measuring them, and a special unit called the Ångstrom unit after a Swedish scientist is most generally employed. And yet food, drugs, checks and paper money, and even crime, must give way before the ultra-violet lamp. The reason lies in the fact that certain chemicals function characteristically when subjected to the ultra-violet rays comprising the wave lengths from about 2800 to 3700 A. U., rays which are not visible but which by these chemicals are stepped down to longer wave lengths resulting in the appearance of color, a phenomenon known as fluorescence. Inorganic chemicals, generally speaking, are not striking in fluorescent effect, but this property is so common in organic chemicals that we seldom can depend upon this characteristic to establish identity. We may, however, use it to disclose a suspected mixture or impurity; thus we can detect acetone in alcohol; benzoates in food products; or we may distinguish between silk and artificial silk; ivory and celluloid; white lead and zinc white; precious stones and paste; true parchment and parchment paper. G. O.

Spectrum of Rhenium. U. S. BUR. STAND. NOTES. *J. Franklin Inst.*, **211**, 373–4 (Mar., 1931).—W. Noddack and Ida Tacke announced the discovery of rhenium in 1925. By means of one gram of potassium perrhenate, donated by A. V. GROOSE, of the Inst. Tech., Berlin, the Bureau of Standards has made arc spectrum measurements in the region 2300 A. U. in the ultra-violet to 8800 A. U. in the infra-red. Approximately 2000 lines have been discovered, all of which are new to the science of spectroscopy. The existence of rhenium was predicted 60 years ago by Mendeléeff. It is so extremely rare that it constitutes one part in a million million of the earth's crust. J. H. G.

Protective Foods. "A Classic of Science." E. V. MCCOLLUM. *Sci. News Letter*, **19**, 123 (Feb. 21, 1931). (Taken from "The Newer Knowledge of Nutrition," by McCollum, Macmillan, **1918.**)—Attention is called to the fact that there is no perfect food. Certain foods as milk and leafy vegetables, while low in protein, fat, and

carbohydrate content, are important and may be designated as "protective foods." It is suggested that foods be classified according to their physiological function and that the public be taught how to use such a classification in constructing a well-balanced diet. H. T. B.

Our Daily Iron. W. H. EDDY. *Good Housekeeping*, **92**, 116–9 (Mar., 1931).—Mary Schwartz Rose and her associates have recently made a careful study of the food habits of a child for four weeks with especial attention to the iron intake and output. They found this child needed about one-third as much of an iron intake as an adult to balance the loss through excretion. When reduced to milligrams per hundred calories of food, the value is 0.5, which is the same as that for adults. The investigators stated, however, that barely enough to meet the loss sustained was not enough. They advised a fifty per cent higher intake or about 0.75 mg. of iron per 100 calories for children of ages two to five.

It has been found that copper in food in the ratio of one part to sixty parts of iron is necessary for proper assimilation of iron. To prevent anemia the presence of these two metals in the food must be assured and they must be there in the proper ratio to each other and to the caloric value of the food as well. B. C. H.

SCIENTIFIC REVIEWS AND BIBLIOGRAPHIES

The Progress of Radioactivity. S. C. LIND. *Hexagon*, **21**, 55–69 (Nov., 1930).—An outline of the progress in the study of radioactivity and of the fields which radioactivity has opened. H. H. K.

Rheology Index. E. C. BINGHAM. *J. Rheology*, **2**, 10–107 (Jan., 1931).—An index to rheological literature similar to that published in "Fluidity and Plasticity," by E. C. Bingham (McGraw-Hill Book Company), but broader in scope and up to date. The articles are arranged under an author index. E. R. W.

The Colleges in the Popular Magazines. R. E. ANDERSON. *Assoc. Am. Coll. Bull.*, **16**, 494–8 (Dec., 1930).—The third résumé of magazine articles dealing with the subject of higher education in its various aspects for the period covering Nov. 1, 1929–Oct. 31, 1930. G. O.

Sixty Educational Books of 1930. *Natl. Educ. Assoc. J.*, **20**, 141–3 (Apr., 1931).—List prepared by American Library Association and the *Natl. Educ. Assoc. J.* in the Teachers' Department of the Enoch Pratt Free Library at Baltimore. Brief reviews are given. A. E. C.

HISTORICAL AND BIOGRAPHICAL

Reminiscences of Gibbs by a Student and Colleague. E. B. WILSON. *Sci. Mo.*, **32**, 211–27 (Mar., 1931).—A very interesting account of Gibb's teaching at Yale University and of his research. Two early photographs are given. G. W. S.

Richard B. Moore. S. C. LIND. *Ind. Eng. Chem., News Ed.*, **9**, 40 (Feb. 10, 1931).—Obituary. Portrait. G. W. S.

John Winthrop the Younger. *Tech. Rev.*, **33**, 191 (Jan., 1931).—Portrait and short account of his alchemical works. S. W. H.

The Manchester Literary and Philosophical Society. C. L. BARNES. *Nature*, **127**, 408–9 (Mar. 14, 1931).—The Manchester Literary and Philosophical Society, in February, 1781, celebrated its 150th anniversary on Tuesday, Mar. 17. Sir J. J. Thompson delivered an address. An honorary member since 1885, he was presented the Society's Dalton Medal, the last award of which was made in 1919 to Lord Rutherford. The Society is one of the oldest of its kind in existence, and occupies a house which was purchased in 1799. This home of the Society has an unequaled collection of Dalton relics. "Here are to be seen nearly all the crude chemical apparatus with which Dalton worked; his meteorological observations, begun at Kendal, and continued for more than fifty years; many of his papers; an orrery, a planetarium, and electrical appliances; his medals, including the Copley Medal of the Royal Society; and a few articles of personal property.

"Dalton came to Manchester in 1793 as 'professor' of mathematics—in which he had some skill—at the then new Manchester Academy. He joined the Society in 1794, and read more than a hundred papers during his half-century of membership. From 1816 to 1844 he was president, but had previously filled almost all the other offices. He supplemented an exiguous income by taking pupils (at 1s. 6d. a lesson), by lecturing, and writing books. One on "The Elements of English Grammar" (1801) is said to have given him special satisfaction. Though none but caretakers ever lived in the house, Dalton was allowed the free use of a room in it, and a marble tablet commemorates the fact that here, out of his experiments and cogitations, the atomic theory was developed."

One of Dalton's pupils was James Prescott Joule. There have been other illustrious members and the Society has played a very noted part in the scientific life of Manchester. F. B. D.

Vulcanization of Rubber. "A Classic Invention." ANON. *Sci. News Letter*, **19**, 154 (Mar. 7, 1931). (Taken from "Gum-Elastic and . . . Vulcanization," by Chas. Goodyear, published by the author at New Haven in **1853.**)—Even though he was just a step from poverty throughout much of his experimental work on rubber, Goodyear retained his faith in the utility of rubber and continued his experiments until he finally hit upon the process known as vulcanization in which the rubber is treated with sulfur and heat. This process has made rubber indispensable. H. T. B.

Zinc, Cadmium, and Mercury. "Classics of Science." *Sci. News Letter*, **10**, 75–6 (Jan. 31, 1931).—Three "classics of science" are here brought together under one caption. The account of mercury and its ore, cinnabar, is taken from Sir John Hill's book, "Theophrastus' History of Stones," published in 1774. Theophrastus is said to have written about 300 B. C.

"There are two kinds of cinnabar," so Sir John says, "one native, the other factitious; the native is found in Spain and is hard and stony. . . . . The factitious is from a country a little above Ephesus. . . . . It is only a sand, shining like scarlet. . . . . (Quicksilver) is obtained from cinnabar, rubbed with vinegar in a brass mortar with a brass pestle."

Zinc is presented by Arthur Edward Waite in two volumes published in 1894 and entitled "The Hermetic and Alchemical Writings of Aureolus Philippus Theophrastus, Bombast of Hohenheim, called Paracelsus the Great." After a paragraph each upon "mixed metals" and "spurious metals" he says, concerning zinc "many metals are adulterated in it. The metal itself is fluid, because it is generated from three fluid primals. It does not admit of hammering, only of fusion. . . . . It does not admit of admixture; nor does it allow the fabrication of other metals." This account is presumed to have been written about 1530 A. D.

"New Details Respecting Cadmium," by M. Stromeyer, is taken from "Annals of Philosophy," Vol. 14, published in 1819. The account is translated from the *Annalen der Physik*. M. Stromeyer communicated his findings, summarized in the paragraphs under abstract, to the Royal Society of Göttingen on Sept. 10, 1818. They had to do with "The new metal which he discovered in zinc and its oxides and to which he has given the name of cadmium."

After describing his method of separating the cadmium ore from that of zinc and of his reducing it by lampblack, he reviews its properties. Included are its bluish gray color, luster, octahedron crystal form, softness, and flexibility. Chemically it is said to tarnish but little in the air, but to burn readily. It is readily soluble in nitric acid and evolves hydrogen when put in other acids. B. C. H.

EDUCATIONAL MEASUREMENTS AND DATA

Pre-College Guidance of High-School Students. M. SCHLICHTING. *Univ. Neb. Educ. Research Record*, **3**, 117–30 (Feb., 1931).—This paper represents a study of the practices in 317 high schools in assisting their students to make articulation with college work.

Of agencies which offer this assistance, the one most used is college representatives and in decreasing frequency; deans, homeroom teachers, a committee, the vocational director, senior counselor, and various organizations.

The method of assisting is, in order of decreasing frequency; by college catalogs, faculty conferences, college visitation, lectures, college bureaus, return of graduates, local contacts, follow-ups, and information blanks.

Topics discussed in these guidance efforts include: college entrance requirements, college to choose and courses to take, college life, and expense of college attendance.

College activities welcomed by high schools include: college open house, college publicity teams, high-school principal's visiting day with his former high-school pupils who are in college, advanced registration for college by high-school authorities, and summer camps or sessions for prospective freshmen.

Two motives are said to actuate colleges in their efforts toward pre-college guidance: to encourage only those students toward college who will profit most from its education, and to give such students a true conception of college life and ideals. B. C. H.

An Analysis of the College Entrance Examination Board Examinations in Elementary Chemistry, for 1921 to 1928. J. W. BOORSTEIN. *Science Educ.*, **15**, 91–100 (Jan., 1931).—A study (*a*) for the analysis of examinations from 1921–28 for comparison with a similar analysis made by H. L. Gerry of 1911–20 examinations; (*b*) a study of the

topics stressed and their percentages; (*c*) whether there is introduced an element of correlation between the science and the everyday experience of the pupils. The present investigator does not find that examinations are being changed very materially.

J. H. G.

A Study of the Scholastic Record of Students Dropped from a College of Education. R. T. GREGG. *Phi Delta Kappan*, **3**, 137–43 (Feb., 1931).—This paper is a report upon 342 students who were dropped from the College of Education of the University of Illinois between the years 1919–29.

Some interesting facts gleaned from this study are: (1) The percentage, two and three-tenths, of the students dropped was of the total enrolment and was quite constant through the ten-year period. (2) Sixty-three and seven-tenths per cent of the students dropped never returned to the university. (3) Forty-seven and six-tenths per cent of those who were readmitted were again dropped. (4) Only nine and seven-tenths per cent of these students dropped finally graduated from the university. Of these who graduated, sixty and six-tenths per cent were in school longer than eight semesters. (5) The financial loss, estimated at twenty-five dollars per credit hour, suffered by these students exceeded one hundred thousand dollars. B. C. H.

A Study of Attendance in Certain Accredited High Schools of Nebraska. A. A. REED. *Univ. Neb. Educ. Research Record*, **3**, 1–4 (Oct., 1930).—In this paper are summarized reports from 320 high schools and for 95,210 pupils in 1918–19 and for 118,953 pupils in 1929–30. The most striking fact brought out by the study, which compares enrolments of 1918–19 with that of 1929–30, is that the high schools are holding their students to the end of the four-year course in a manner not known ten years ago.

For the schools included in the report the ratio of ninth-grade enrolment to tenth-grade enrolment to eleventh-grade enrolment to twelfth-grade enrolment for 1918–19 was 38 to 25 to 20 to 17 while for the same schools for 1929–30 the ratios of enrolments were 30 to 26 to 23 to 21, respectively.

Put in another way, in 1923 the senior classes in the 320 high schools contained 60 per cent of the 1919 entering ninth-grade students, while in 1930 the senior classes of these high schools contained 69 per cent of the entering ninth-grade for 1926. The ratio for grade-school enrolment to high-school enrolment changed from 63 to 21.2 in 1918–19 to 56.5 to 27.7 for 1929–30. B. C. H.

Arithmetical and Algebraic Processes as Sources of Student Difficulty in University Courses. H. F. HALD. *Univ. Neb. Research Record*, **3**, 35–6 (Oct., 1930).—In an effort to determine what processes were troublesome a questionnaire for each subject was worked out and submitted to thirty-three professors in seventeen departments of the University of Nebraska. Laboratory assistants in six departments were also interviewed. From information thus gathered a test was devised for each subject so that it would reveal the degree of preparedness of the students for the types of difficulty they are likely to meet in college.

Among Miss Hald's findings are: the algebraic processes are used predominantly in the sciences; of all the difficulties reported, 80 per cent were arithmetic; the elements needing attention, according to the professors, were relatively few, twenty-one in number. B. C. H.

The Costs of Medical Education. Students' Expenditures. R. G. LELAND. *J. Am. Med. Assoc.*, **96**, 682–90 (Feb. 28, 1931).—"The cost of medical education to the student for 1929–30 shown by the reports of 1161 students attending widely separated and various types of medical schools averages slightly more than $1100. Tuition and fees and board and room call for 59 per cent of the average total expense. Costs seem to be highest in the schools of the New England and Middle Atlantic states and most reasonable in the schools of the Pacific and Mountain states, with the South Atlantic states following closely." S. A. L.

THE PHILOSOPHY OF EDUCATION

The Future of the Liberal College. R. L. KELLY. *Assoc. Am. Coll. Bull.*, **16**, 443–52 (Dec., 1930).—There are many forces "impinging" upon the liberal college, but America demands many schools of many kinds for her people and is especially interested in the schools devoted to liberal education. That the liberal college has a future seems certain since there is a demand for broader and richer content in the education of Americans. The future of such colleges, however, will be largely determined by the spirit of the age in which they find themselves. The reaching down of research methods into the undergraduate colleges is a sign of the new day. Research demands a period of preparation, and yet the demand is already strong for the shortening of this period.

How can both of these demands be met? Research workers are already advising the elimination of the needless duplication of subject matter—22.8% of history taught in college repeats that taught in high school; there is a 29% repetition of science studies; and 38% in social sciences. G. O.

Modern Youth and the Research Spirit. J. O. HERTZLER. *Sci. Mo.*, **32**, 256–63 (Mar., 1931).—There is no place in this modern world for the person who acts only on the basis of instinct, habit, and routine. Education, therefore, must consist of more than an accumulation of standardized facts. It must develop the powers that will give the individual facility to use acquired knowledge and technic, and must produce a capacity for interpretation. H. contends that it is necessary to give students the research spirit in order to produce these results. In the research spirit there is a discipline which produces facility in analysis, interpretation and conclusion, and develops in the individual new powers of imagination and inventiveness. In a civilization so intricate and changing as ours, the spirit of research alone will enable us to distinguish the abiding, the socially and culturally sound from the opulent, the standardized, advertized and futile. The changes in science itself, and the uses and misuses of science necessitate the research spirit if the citizen is to evaluate these changes properly and make the requisite adaptations. Research in the fundamental sciences is continually making changes in specialized technical callings. To be successful in these callings, therefore, one must be able to incorporate the new findings and technics into one's own practice. Social situations over which ethics presides as regulator are changing continually and along fundamental lines and in order to make an intelligent orientation of ethical ideas and arrive at justifiable conclusions, one must have the research spirit. G. W. S.

Current Trends in Higher Education. E. H. WILKINS. *Bull. Am. Assoc. Univ. Profs.*, **17**, 152–9 (Feb., 1931).—The author lists six trends: (1) the break up of the four-year unit, (2) growing distinction between general and special education, (3) general education becoming more complete, (4) achievement of a real mastery in special education, (5) increasing individualization, (6) general improvement of higher education.

Extended comment is offered upon the last two only. "It is a mistake," says the author, "to assume that the small college assures individual attention." The larger institution may just as truly individualize its service to its students if it has a faculty that is proportionate to the number of students and has the good-will toward and concern for the students. Friendly guidance recognizing intellectual, social and ethical needs should be the privilege of every individual student. College administrators should recognize the time demands of such service from teachers.

Concerning the sixth trend, it is stated, "Higher education is improving more speedily and more thoroughly just now than has ever been the case before." Some weaknesses imputed to college teaching are: it is traditional rather than unique or original, it assumes an aloofness that does not brook criticism, and through it all there is a smug complacency which does not countenance suggestion toward improvement. B. C. H.

PROFESSIONAL

Does the Teaching of Science Make Teachers Scientific? J. MOUNT. *Wash. Educ. J.*, **10**, 198–9, 220 (Mar., 1931).—Popularity of certain high-school science courses depends in part upon the teacher. Certain teachers teach only fundamental science, which is beneficial solely to the good student. Others use methods of memorization and imitation which enables the duller student to appreciate the application of science in everyday life. The choice of the use of the lecture-demonstration method or individual laboratory-work method is based upon insufficient premises, also the value of oral recitation. Some teachers stock their libraries with interesting scientific readings, others do not. The author concludes that high-school science teachers are not alike in their "likes." A. E. C.

Who Makes Teachers Cranky? *World's Work*, **50**, 33–4 (Mar., 1931).—Experts make teachers cranky. Why? Because they have made teaching a pursuit of graduate degrees, of graduate courses. They have made the schoolroom a place to sell tickets to children who are ashamed to refuse to buy them. "Our modern school programs, with their enrichments, their extra-curricular activities, their guidance which does not guide, and their orientation which does not 'orient,' may be short cuts to the promised land, but I doubt it. . . . . Experts multiply like the seven-year locusts and they flourish like the green bay tree. . . . . So many superintendents must have something to do. . . . . They devise many a 'hell of a fine thing'. . . . . Sooner or later the public is going to learn just how fine some of these things are." J. H. G.

Research and Productive Writing in Oberlin College. C. G. ROGERS. *Assoc.*

Am. Coll. Bull., **16**, 456–61 (Dec., 1930).—For a number of years there has been in Oberlin College a committee of the faculty on scientific research. The science members of the faculty realized, however, that research and productive work of other sorts may be a proper function of the college in all of its departments and should not be limited to the natural sciences. They, therefore, recommended the establishment of a standing committee on reproductive work to stimulate and foster interest in productiveness upon the part of members of the faculty in all departments. During the past academic year, the science departments attempted to acquaint the Committee on Productive Work with the research work of all the science departments through a series of research demonstrations, each department having an "evening at home" with the staff and student members. For the encouraging of productive work there is included a sum in the annual budget (at present $2000) to be expended in grants of varying amounts from $10 to $500 for various research projects. These amounts were spent for clerical assistance, traveling expenses, photographic and photostatic reproductions, and the manufacture of special equipment which could not be secured in the open market. Realizing that research demands time, one may also receive a leave of absence for a semester or a year to complete a piece of work, or an allowance of time in the teaching schedule. Such an allowance will make an addition to the college budget, but it will give the teacher continuous opportunity for investigation which he craves and incidentally place upon him the burden of demonstrating whether he deserves such consideration. G. O.

CONTEMPORARY NEWS AND COMMENTS IN CHEMISTRY AND EDUCATION

Yale Institute of Human Relations and the Human Welfare Group. B. W. SHIMP. *Assoc. Am. Coll. Bull.*, **16**, 453–5 (Dec., 1930).—The Welfare Group at Yale is an association of schools and departments concerned with the study of human behavior. To the Institute may belong any member of the university whose interests in the fields of biology and sociology can contribute to the object of the Institute. According to Pres. Angell, they hope to train men who should be able to take their places either in the professions or in business life with a more sympathetic appreciation of the essential facts regarding human nature and the social order in all its economic and political phases. G. O.

Hoosier Educational Facilities. ANON. *Ind. Eng. Chem., News Ed.*, **9**, 33–4 (Feb. 10, 1931).—A brief description of schools of higher learning in Indiana. G. W. S.

Some Chemical Research Laboratories in Indianapolis. ANON. *Ind. Eng. Chem., News Ed.*, **9**, 51–2 (Feb. 20, 1931).—A brief description of commercial research laboratories in Indianapolis. G. W. S.

The Manchester Literary and Philosophical Society. See this title, page 1202.
Chemistry at Purdue University. See page 1208.
Preliminary Announcement, Buffalo Meeting of the A. C. S. See page 1215.
Award Offered for Research in Education. See page 1216.
Dr. Kelly Appointed to Office of Education. See page 1216.
Ninth Colloid Symposium at The Ohio State University. See page 1218.
Professor Freudenberg Talks under Two Dohme Lectureships at Hopkins. See page 1220.
Potash Center May Shift to Italy. See page 1220.
Merck and Co., Inc., Renews Analytical Fellowship at Princeton. See page 1221.
International Fellowships for Research. See page 1221.
Cold of Liquid Helium Gives Very Conductive Metals. See page 1221.
Flour from Fish Makes Human Food. See page 1222.
Atom Nucleus Yields Secrets to Bombardment. See page 1222.
Magnesium Starvation Found to Cause Death. See page 1223.
Chemical Developments Reported at the Indianapolis Meeting of the A. C. S. See page 1224.
Part of Cosmic Rays May Come from Sun. See page 1225.
Knife-Marked China Investigated by Scientists. See page 1226.
Music of Alcohol on Radio. See page 1226.
Dr. Mendenhall Describes Changes in Behavior of Free Electrons. See page 1227.
New Drug Relieves Pain of Lead Colic, Gallstone Colic. See page 1228.
Find Way to Eliminate Danger in Serum Treatment. See page 1228.
Second International Congress of the History of Science and Technology. See page 1229.
Dr. von Weimarn Honored in Osaka. See page 1229.

Science Headquarters May Overshadow Westminster Abbey. See page 1230.
Chemical Books of Historic Interest Found in Bodleian Library. See page 1230.
Visiting Professors to Teach in Summer School of The Ohio State University. See page 1231.
Maltbie Chemical Company Continues Research Fellowship at Philadelphia College of Pharmacy. See page 1231.
Sioux Valley Chemists Club Meets. See page 1231.
Professors Davis and Cleaveland to Lecture at Western Reserve Summer Session. See page 1231.
Dr. McMaster Completes Twenty-Five Years at Washington University. See page 1232.
The District of Columbia Association of Chemistry Teachers Meets. See page 1232.
Institute of Metals Will Meet in Switzerland. See page 1232.
Deutsche Bunsen Gesellschaft. See page 1233.
Intercollegiate Student Scientific Conference at Mount Holyoke. See page 1233.
Engineers' Day at Washington University. See page 1234.
University of Maryland Fourth Biennial Chem Sho. See page 1234.
Dr. Buehler Addresses the Ira Remsen Society of the Missouri School of Mines. See page 1235.
Winners of 1930-31 Prize Essay Contest for Colleges, and Normal Schools and State Teachers' Colleges. See page 1235.

GENERAL

Kodacolor Motion Pictures for the Amateur. G. E. MATTHEWS. *Hexagon*, **21**, 115–22 (Dec., 1930).—An illustrated description of the process of making and developing colored motion pictures taken with a simple camera. H. H. K.

A Comparison of Colored and Uncolored Slides, II. W. P. MACLEAN. *Educ. Screen*, **10**, 41 (Feb., 1931).—In general, the addition of color to a slide emphasizes the object colored. Where the dominant visual experience desired is natural scenery, or combination of natural and artificial scenery, color is a distinct advantage. Where the visual experience desired is mainly one of spatial relations, architectural detail or people in action or repose, color is of little value. It appears that judgment must be used in the use of color on slides to be used in secondary schools in order that attention may not by coloring be directed away from the very thing sought. H. T. B.

Science and the Supernatural. A. J. CARLSON. *Science*, **73**, 217–25 (Feb. 27, 1931).—"As I see it, the supernatural has no support in science, it is incompatible with science, it is frequently an active foe of science. It is unnecessary for the good life. And yet, the supernatural, in varying dilutions, is likely to persist in society for a very long time. The unconditioning and reconditioning of mankind in fundamentals has shown a slow progress in the past. It may go a little faster in the future. It is a matter of forgetting the hypothetical universe created out of ignorance and motivated by our undisciplined emotions; and a reconditioning to the actual universe, as gradually understood through controlled experience and experiment." G. H. W.

Radium Rays Three Times More Effective than X-Rays. Though radium rays and X-rays cause reddening of the skin to the same extent, the radium is about three times more effective in producing deep-seated effects. This is the conclusion recently announced to the Optical Society of America by Dr. G. Failla and P. S. Henshaw of the New York Memorial Hospital.

This work has required the development of an apparatus which would measure equivalent, comparable doses of the two radiations. It was found that 500 Röntgen units of radium gamma rays produced the same reddening of the patient's skin as 600 Röntgens of filtered X-rays.

Other experiments were made on wheat seedlings. In both cases the effect of the radiation is shown as a stunting of the shoots and roots. Three times as much X-radiation was required in this case to produce equal effects. For this reason it may be desirable to use higher voltages with X-rays for medical purposes.

Dr. Failla emphasized that the suitability of a certain type of rays for a given tumor must always be taken into account.—*Science Service*

Contemporary News in Chemistry and Education

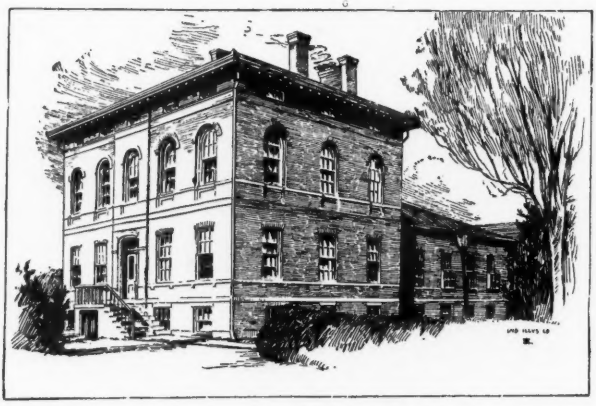
CHEMISTRY AT PURDUE UNIVERSITY

M. G. MELLON AND L. A. TEST, PURDUE UNIVERSITY, LAFAYETTE, INDIANA

Historical Development*

Purdue University was established as a land-grant college under the Morrill Act of 1862 and first opened its doors to students in 1874 as a technical and scientific school. That the value of chemistry in such a school was early recognized is evidenced by the fact that, from the beginning, the science occupied an important place in the curriculum. A four years' course with postgraduate work was outlined, although only one term of study was required at first for graduation. It was announced in the catalog that "A large part of the student's time is concerned in the laboratory work, the plan of instruction proposing to combine the theory and practice of chemistry in such a way as is best calculated to develop intellectual powers and secure accuracy of knowledge."

The new institution was fortunate in securing the services of HARVEY W. WILEY, later the well-known chief of the United States Bureau of Chemistry, for its first professor of chemistry. Professor Wiley began his duties in 1874 and at once, by his energy and enthusiasm, made the department one of the strongest in the university. At this time the department of chemistry shared with the department of art the first floor of the Science Building, a small two-story brick structure on the west side of the campus, shown in the accompanying illustration. The second story of this building housed the department of physics, while the entire school of engineering found ample quarters in the basement. When the department of pharmacy was organized a few years later, it also shared the building.



VIEW OF THE BUILDING IN WHICH HARVEY WILEY STARTED THE WORK IN CHEMISTRY AT PURDUE UNIVERSITY

In 1880 Professor Wiley became state chemist as well as professor of chemistry. Associated with him at this time was H. A. HUSTON, afterward state chemist for a number of years.

* Written by L. A. TEST.

Professor Wiley resigned in 1883 and PROFESSOR R. B. WARDER, later of Howard University, was secured to fill the vacancy. The department continued to grow under the new head, and it was during this period that the department of pharmacy was organized. He was with the institution as professor of chemistry and state chemist for four years, being followed in 1887 by DR. JOHN ULRIC NEF, later well known as head of the department of chemistry at the University of Chicago. Professor Nef served from 1887 to 1889 when he was called to Clark University. Many of his researches on the structure of quinone were carried out while at Purdue. It was during this time that the new Mechanical Laboratory was built.

Upon the resignation of Professor Nef in 1889, WINTHROP ELLSWORTH STONE, who had recently taken his doctorate at Göttingen, was called to take charge of the department, a position he held until he became president of the university in 1900.

The institution was growing rapidly at this time and by 1893 the department of chemistry had entirely outgrown the old Science Hall. In this year Heavilon Hall, the new building for mechanical engineering, was completed, which allowed the departments of chemistry and biology to move into new quarters in the old Mechanical Laboratory, remodeled for their purpose to provide room necessary for increasing enrolments. They occupied this building jointly for a number of years.

In 1895 PERCY NORTON EVANS, a graduate of McGill University who had just taken his doctorate at Leipzig, joined the chemical staff as instructor in analytical chemistry. When Professor Stone became president in 1900, Dr. Evans was made head of the department of chemistry, a position he held until his death in 1925.

With the greatly enlarged quarters and the increased facilities for laboratory work, the department grew rapidly, new members were added to the staff, new courses offered, and the enrolment grew steadily, so that by 1906 the building planned for two hundred students was accommodating over four hundred, and plans were prepared for a much-needed new building. At a cost of $70,000 this new building, designed to accommodate about twelve hundred students in chemistry, was erected on the west side of the campus near the site of the first science building, at that time occupied entirely by the department of pharmacy. In the autumn of 1907 the department moved into the new building, the first on the campus to be built for, and occupied entirely by, the department of chemistry.

Professor Evans' death occurred just after the close of school in 1925. PROFESSOR A. R. MIDDLETON, who had joined the department in 1906 and who was senior member of the staff, became acting head.

Late in the summer of 1926 DR. RICHARD BISHOP MOORE, late of the United States Bureau of Mines and internationally known for his work with radium and helium, was chosen to become dean of the School of Science and head of the department of chemistry.

Under the administration of Dean Moore the scope of the department was extended and the courses in graduate study increased. This, together with the greatly increased demand for scientific education following the World War, so increased the enrolment in the department that the building planned for twelve hundred students was soon occupied by two thousand with a chemical staff of over forty. It became necessary to excuse large numbers of beginning students from the laboratory work. In order to care for this large enrolment and to provide for the increased number of graduate students, it became imperative that a new building which would at once care for two thousand freshmen and many graduate students and which would contain ample accommodations for many years to come, must be planned. Dean Moore

threw himself into this new project with his characteristic energy and the fall of 1930 found the department occupying the first unit of the building described below. Unfortunately, Dean Moore's illness and death a few months after the occupation of the new laboratory deprived him of the pleasure and satisfaction of working in the building which had cost him so much time and energy to obtain.

On Dr. Moore's death, Professor Middleton again assumed charge of the affairs of the department.

The present professorial staff includes A. R. MIDDLETON, L. A. TEST, R. H. CARR, R. E. NELSON, M. G. MELLON, R. F. NEWTON, THOS. DEVRIES, H. B. HASS, AND R. C. CORLEY. Others who have served similarly in the past include WALTER JONES, W. H. TEST, J. H. RANSOM, E. G. MAHIN, N. E. LOOMIS, AND F. O. ANDEREGG.

The New Laboratory*

Late in 1927 the Trustees approved the proposal for a new laboratory, and the writer was given the assignment of making plans and of watching construction work. The structure designed is intended to provide only for the work of the department of chemistry, as specialized phases of chemical work, such as those in agriculture, home economics, pharmacy, and chemical engineering, are located in other parts of the university.

In presenting this general description of the building there is no thought that anything essentially novel in construction of laboratories is included. The chief merit of the general plan lies perhaps in the fact that it represents a different arrangement of the various features which are thought by most teachers and research workers to constitute necessary parts of a modern building for educational work. Probably only experience with these features will demonstrate whether the scheme is any advancement over that used in other large laboratories. Undoubtedly even then the verdict would be largely dependent upon the personal prejudices of the individual making the observations.

* Written by M. G. MELLON.

GENERAL PLAN

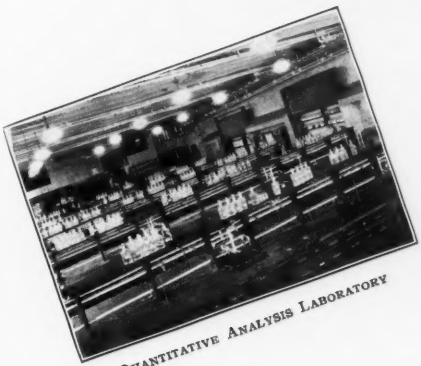
The structure, with its three double doors, as it will appear when completed, is illustrated in the accompanying architects'** sketch. At present only the first unit is completed, although the plans were made for the entire building. The other four entrances are located, two at each end, at the ends of the long corridors. Two of these end doors are shown in the photograph of the first unit. The general arrangement of the various parts of the building is shown in a previously published cut of the second floor plan.† One might state that, looking from front to back, there are roughly two block E letters, the horizontal bars of the first extending to the class and small lecture rooms in the center of the building. This gives a combination of open- and closed-court construction. Those familiar with other large laboratories in this country will recognize an adaptation and recombination of arrangements in use at other places, particularly Cornell University, the State University of Iowa, and Michigan State College. In addition to the full four floors there is an attic, and a service basement under part of the building. The basement corridor extends completely around the building and is essentially a tunnel for service lines.

Going more into detail, one finds at the back of the building, in the three horizontal bars of the rear block E, provision for all the large laboratories, arranged one above the other. In general, these are devoted to the elementary and undergraduate courses having large enrolments. With the dispensing and store rooms located in this portion of the building, the heavy traffic of large numbers of students is minimized as much as possible. It will be noted that the two large labora-

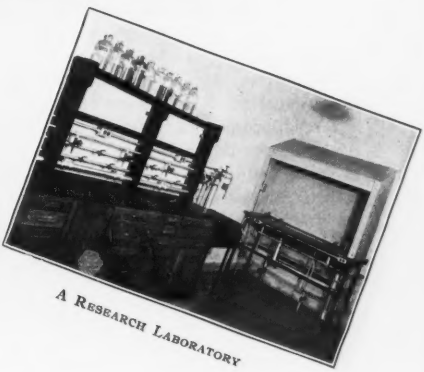
** Architect, WALTER SCHOLER, Lafayette, Indiana, and consulting architect, A. N. GIBB, Ithaca, New York.

† MELLON, M. G., "Purdue University's New Chemical Laboratory," 7, No. 20, 1 (Oct. 20, 1929).

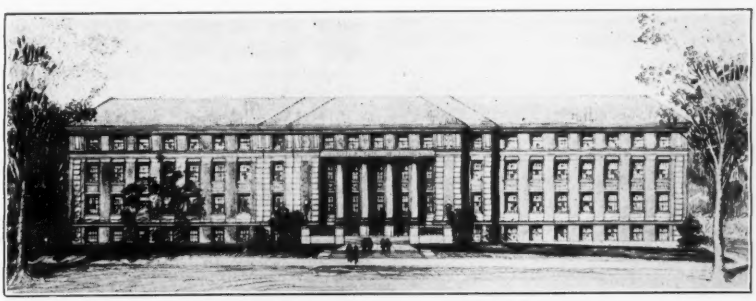
THE FIRST UNIT



QUANTITATIVE ANALYSIS LABORATORY



A RESEARCH LABORATORY



ARCHITECTS' DESIGN

CHEMISTRY BUILDING OF PURDUE UNIVERSITY

tories in the corners are divided by a partition running lengthwise. This consists largely of flues extending from wall hoods on each side of the partition and from all four floors to the exhaust fans in the attic. The arrangement represents a compromise between the very large elementary laboratories at Cornell University and the small ones at Michigan State College. There are lockers for a maximum of seventy-two students per section in general chemistry or thirty-six in quantitative analysis in each side of the divided laboratory. At the ends of the building are somewhat smaller laboratories for advanced undergraduate and graduate work. It is probable that one or more of these may have to be taken later to provide a larger number of rooms for recitations. The whole section of the building across the front is given over primarily to small rooms for offices and research laboratories. Here the partitions are such that they may be removed to throw two or more of these rooms together without serious disturbance of any equipment or service lines. A number of similar laboratories, differing somewhat in size, are located at the back or facing the closed court. In the front the small rooms are either 10 or 13 feet wide and 21 feet long. Two special provisions are found in this part of the building. On the third floor, directly over the main entrance, is the space assigned to the reading and stack rooms of the departmental library. Adjoining the latter is a small seminar room. On the fourth floor the section over the library is designed as a room for the general social use of the members of the chemical staff. The cases for displays are found either in recesses in the end corridors or in the wide portion of the front corridor near the entrances to the main lecture room.

All the recitation and lecture rooms now planned are located in the portion of the building around the closed court, artificial light seeming least objectionable for classes. As far as feasible, all the laboratories are located around the outside of the building. Above the first floor each floor has two small rooms for recitations and a small lecture room seating ninety-eight. The large- and intermediate-size lecture rooms, seating, respectively, four hundred sixty and one hundred eighty, are on the first floor, with the main entrance to the former on the second floor, directly across the corridor from the main entrance to the building. The large lecture room includes a balcony seating one hundred two, the entrance to which is on the third floor. In all the lecture rooms the entrances are located so that incoming, late students need not pass the lecture table.

The following data concerning the building may be of interest: dimensions, in feet—length, 251; depth at end, 192; width of outside wings, 67; width of center wing, 44; estimates for the first unit—cubic feet, 900,000; square feet per floor, 13,600; total cost, about $440,000;* and capacity for undergraduate divisions of chemistry—seventeen hundred in general, four hundred in analytical (including qualitative and quantitative analysis and biochemistry), two hundred eighty-five in organic, and fifty-four in physical.

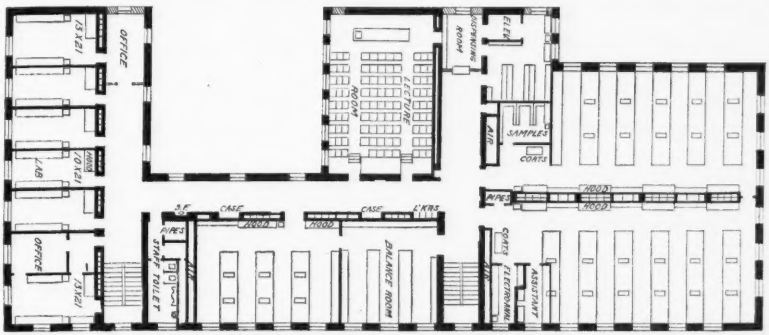
SPECIAL FEATURES

Limitations of space prevent any detailed description of the building, but it is believed the items mentioned below may be of interest.

Structural Features. The exterior is red brick with limestone trimming and tile roof. Across the two ends and the front of the building is a row of names of men prominent in the history of chemistry, one name on each stone spandrel between the second- and third-story windows. The construction of the roof is such that the openings from the exhaust ducts are not visible from the ground level. Provision is made in all rooms for individuals to hang their wraps. In

* This amount is more than a proportionate share of the estimated total cost due to the inclusion of several items which should be shared by all units, such as architect's fee for the complete plans and a number of service facilities which had to be provided of sufficient size for the complete structure.

the main laboratories and lecture rooms a specially designed steel hanger is used. In the class rooms there are on one side of the room behind a blackboard a shelf and row of hooks which may be raised or lowered. These boards are similar to those shown in the picture of one of the main laboratories (p. 1211) and were included so that each room for recitations has blackboards around three sides. In the research laboratories individual, portable steel lockers are provided between the end of the laboratory table and the outside wall. All walls and the ceilings of corridors are plastered while the other ceilings are of painted, concrete beam construction. A recessed bulletin board



PLAN OF THIRD FLOOR, FIRST UNIT

is located near the entrance to each laboratory and lecture room. On each floor is an opening to a waste chute and a closet nearby for the truck used to collect the waste material.

A plan which promises to provide space for a reasonable period in the future having been decided upon, there was encountered the serious problem of making the interior arrangement such that separate units could be built as needed and as funds became available. From this standpoint it is believed the plan adopted merits consideration in at least two respects: the unit arrangement can easily be made such that any one unit is essentially a cross-section of the whole, in that it provides some of all the more generally used rooms, such as large and small laboratories, class and lecture rooms, and offices; and the addition of another unit involves practically no rearrangement of rooms or services already in use. This is illustrated in the accompanying plan of the third floor. Perhaps the most important service feature encountered in making provisions of this kind is the series of dispensing rooms. For example, if one locates an elevator to serve in the first unit, it should be in the proper location to serve as well or better in any later arrangements. Such items are not easily moved from place to place. In this case, when the next unit is added, it will be necessary only to move a short wall to bring the elevator into the larger dispensing room, and to remove the walls (shown shaded) at the ends of the corridors where the latter are cut, together with the partitions which now make of the ends of these corridors either offices in the front or part of the temporary dispensing rooms at the back. The other part of the temporary dispensing room will become a research laboratory in the later arrangement.

Ventilation. The individual down-draft hoods planned for use in certain large laboratories (but temporarily omitted) were designed with the openings facing lengthwise of the desks rather than crosswise so that two students directly across from each other could use the same hood.

To eliminate many of the troublesome turns in the duct work leading from the small rooms on the front to the fans in the attic, a tier of four rooms is grouped on a single fan with dampers to equalize the pull on the different floors. A remote control switch is located in each of the four rooms. Each main laboratory has its own locally controlled exhaust fan emptying directly through the roof. Three fans for fresh air serve different portions of the first unit, and the whole building is similarly planned. All fans are located in the attic. They are the direct-connected type except the large ones supplying fresh air.

Laboratory Equipment. Cross sinks are used in all desks, thus bringing every student beside a sink. One end of the desks in the main laboratories is placed against the outside wall. At the other end is the aisle, along which extends the row of wall hoods and shelves for service facilities. A disappearing sliding seat is provided for each student in all large laboratories. Except in physical chemistry, each student's working space is provided with a removable book support for use on the reagent shelf.* Most desk tops are Alberene stone treated with paraffin. The working space per student varies from 42 inches in general chemistry to 81 inches in quantitative analysis. The lecture rooms are designed for use by one man when showing lantern slides, all equipment, such as window shades, automatic lantern, and lights, being controlled electrically at the lecture table. In the research laboratories the desks consist of two six-foot sections, either (or both) of which is removable, not being connected in any way with the service lines on the wall. Two of the four sections in a room contain a special drawer designed for use as a writing desk.

Plumbing. Both the chemical waste lines and the sinks are chemical stoneware. Plumbing fixtures are ordinary, polished red brass, part of which were given one or more coats of clear lacquer as a protective measure. Each sink in the research laboratories is provided with a cold water-steam mixer designed by the departmental mechanic. Except in the laboratories for general chemistry, each hood is provided with a cast iron hot plate for high-pressure steam, and each student has available a Cenco-Harrington water pump for suction. On each side of the small laboratories four of these pumps may be interchanged with ordinary water nozzles. In these small rooms the reagent shelves, supporting the plumbing, are hung on the wall in six-foot sections. Either the outside one or both may be removed for special work by disconnecting unions. All the main service lines are carried vertically in pipe shafts and horizontally on the ceilings underneath the floor they serve, thus being readily accessible. Sliding trays in the sinks are used for waste material. All piping exposed in the laboratories is painted with aluminum bronze.

Electrical Installation. The following special provisions may be noted in connection with the electrical facilities: an outlet box in the laboratories for research and for physical chemistry, as well as in one hood in certain large laboratories, at which, through a nearby distributing panel, direct current of various voltages or alternating current at 220 volts may be connected; a three-wire system for heavier amperages for research laboratories in physical chemistry; and a trunk-line system at the distributing panels enabling any room with a box outlet to be connected electrically with any other so equipped.

Handling Supplies. The general storage of chemicals is in the basement, whereas glassware is on the ground floor. There is a dispensing room on each floor, connected (in the final plans) by an inside stairway, an elevator, and a dumb-waiter electrically controlled. Since certain kinds of courses are segregated, such as analytical chemistry on the third floor, the material specially needed for such

* M. G. MELLON, "A Book Support for the Chemical Laboratory," *School Sci. Math.*, **29**, 728–30 (1929); *cf.* J. CHEM. EDUC., **7**, 191 (Jan., 1930).

work, together with certain general supplies, is kept on that floor. Each dispensing room has a small work space with sink, a hood, and a special fireproof closet for storing fuming or dangerous chemicals. Keys or combinations for padlocks for lockers on a given floor are handled at the dispensing room on that floor.

PRELIMINARY ANNOUNCEMENT, BUFFALO MEETING OF THE A. C. S.

Program

The 82nd meeting of the American Chemical Society will be held in Buffalo, N. Y., Aug. 31–Sept. 4, 1931. Monday of convention week will be devoted in the morning to a meeting of the Council and in the afternoon to a general program of papers describing some of the new tools of research. The remaining sessions on Tuesday and Wednesday will be in charge of the various Divisions.

On Tuesday morning the program of the Division of Chemical Education will feature a joint symposium with the History of Chemistry Division, on "The History of Chemical Education in America." It is planned to make this symposium a memorial to Edgar Fahs Smith who was the first chairman of this Division ten years ago, and who was also chairman of the Division of History of Chemistry. The symposium program will consist of the following invited papers:

1. L. C. NEWELL, Period up to 1820.
2. C. A. BROWNE, Period from 1820 to 1870.
3. HARRISON HALE, Period from 1870 to 1914.
4. F. B. DAINS, Period after 1914.

The semi-annual Division luncheon will be held Tuesday noon. Wednesday morning will be devoted to a meeting of the Senate and to meetings of standing committees, while the afternoon program will be limited to papers on Visual Aids in Chemical Education. Miscellaneous papers will be assigned to the Tuesday afternoon and Thursday morning sessions. The annual business meeting will be held at the close of the latter.

Exhibits

High-school classes everywhere are invited to send exhibits to the Buffalo meeting. A prize of $10.00 is offered by the Division for the best one submitted. Free space will be reserved on request to the *Local Secretary* of the Division, but each exhibitor must assume all costs of packing, transportation, breakage, and loss.

Papers

Papers for the symposium "The History of Chemical Education in America" and "Visual Aids in Chemical Education" will be by invitation. Authors of miscellaneous papers are earnestly requested to coöperate as follows:

1. Submit as soon as possible the titles of proposed papers, together with abstracts in duplicate and an estimate of the minimum time required, exclusive of discussion. It is the seasoned opinion of members of the Division that, since the time is limited, an author should read only an abridgment of his paper, comprehensive enough to stimulate discussion, reserving the complete paper for publication.
2. The name, address, and professional connection of each co-author must accompany the title.
3. The complete manuscript and abstracts must reach the *Secretary* prior to July 15th in order to be included on the Buffalo program. Papers received after this date will be held over, with the authors' consent, for a subsequent meeting.
4. Organize significant features on slides, films, or in mimeographed form for distribution at the meeting. These devices enhance the value of any paper. However, the amount of material on any one slide should be strictly limited.
5. Do not send in a title unless you expect to be present to read your paper.

By vote of the council of the A. C. S., papers by American chemists who are not members of the A. C. S. shall not appear

on the program unless they be joint papers with Society members and no paper may be presented at a meeting unless the title has been printed in the final program. Papers read before the Division become the property of the Society, and, if acceptable for publication, will appear later in the JOURNAL OF CHEMICAL EDUCATION. No paper already submitted for publication in other journals should be offered for the program.

R. A. BAKER, *Secretary*
College of the City of New York
17 Lexington Avenue
New York, N. Y.

AWARD OFFERED FOR RESEARCH IN EDUCATION

Kappa Delta Pi, an honor society in education, announces its Research Study Series with a biennial award of one thousand dollars for the study adjudged most meritorious in a given field. The award for 1931–32 will be given for the best report of research dealing with "The Measurement of Efficiency in Teaching." The following conditions govern the participants and those making the award:

(1) No single method of investigation is specified. The research may be experimental, statistical, or philosophical in character. The pertinency of the method to the phase of the problem studied will be considered in judging the reports.

(2) The basic criteria in judging the worth of a report will be its contribution toward the solution of the problem, the validity of the technics employed, and the organization and literary merits of the report.

(3) The reports submitted in competition will be judged first by the Executive Council of Kappa Delta Pi. The three, four, or five reports (depending upon the total number received) adjudged to be best will then be submitted to a committee of members of the Laureate Chapter of Kappa Delta Pi and consulting specialists, who will select the winning report. The Laureate Chapter members are JOHN DEWEY, F. P. GRAVES, HELEN T. WOOLLEY, E. A. PARK, E. L. THORNDIKE, W. W. CHARTERS, CHARLES H. JUDD, E. P. CUBBERLEY, J. E. RUSSELL, F. W. BALLOU, SUSAN M. DORSEY, L. M. TERMAN, E. A. ALDERMAN, P. H. HANUS, SIR JOHN ADAMS, PAUL MONROE, HENRY SUZZALLO, W. C. BAGLEY, LOTUS D. COFFMAN, PAYSON SMITH, and W. H. KILPATRICK.

(4) The report which receives the award will become the property of the society, and will be published by the society in a monograph series complementing the present Kappa Delta Pi Lectureship Series. The society may publish in the monograph series, or, in abridged form, in the *Kadelphian Review*, meritorious reports submitted in the competition which are not awarded a prize. Such publication would be without expense to the author.

(5) The society reserves the right to reject all reports if in its judgment none is sufficiently worthy of an award, and to divide the award between two contestants in the event that two reports have apparently equal merit.

(6) The competition is open to any one, anywhere—but all reports submitted must be in the English language.

(7) Manuscripts submitted for the 1931–1932 award should be in the hands of the recorder-treasurer of the society on or before September 1, 1932. Announcement of the award will be made at the annual dinner of the society in February, 1933.

Further information may be obtained from E. I. F. WILLIAMS, recorder-treasurer, Executive Council of Kappa Delta Pi, Heidelberg College, Tiffin, Ohio.—*School and Society*

DR. KELLY APPOINTED TO OFFICE OF EDUCATION

DR. RAY LYMAN WILBUR, Secretary of the Interior, has announced the appointment of DR. FREDERICK J. KELLY, professor of higher education at the University of Chicago, to be chief of the section of colleges and professional schools in the Office of Education. He succeeds DR. ARTHUR J. KLEIN, who is now professor of school administration at The Ohio State University.

Dr. Kelly has been a teacher, superintendent, dean of both education and administration, professor of research and higher education, university president, and participant in higher education surveys.

In addition to directing and supervising the work of specialists and clerks in the college and professional school section of the Office of Education, Dr. Kelly will organize and direct various research studies, including survey of land-grant colleges and of state systems of higher education, and will make comprehensive studies of higher educational institutions. He will initiate and organize national and regional conferences of university and college executives. These conferences will consider and formulate educational and administrative policies relating to the several fields of higher education. The new member of the Office of Education staff will also serve as a consulting specialist to university and college presidents on na-

A. C. S. GUESTS AT THE DEDICATION OF THE NEW CHEMISTRY BUILDING OF INDIANA UNIVERSITY

The American Chemical Society was represented at the dedication of Indiana University's new chemistry building on April 2 by an informal delegation which surpassed all expectations in point of size. A fleet of motor buses was provided for the trip and the local weather man coöperated by providing the first sunny day of the convention week. En route to the Indiana campus visits were made to a limestone cutting and fabricating plant and to a limestone quarry. Luncheon at the University furnished an enjoyable sequel to the riding and walking of the morning.

The afternoon's events were as announced in the program [J. CHEM. EDUC., **8**, 752–3 (Apr., 1931)], with the exception that DR. WHITMORE had been called home because of the death of his mother. DR. L. M. DENNIS spoke briefly in his stead.

A somewhat hurried informal inspection of the building was all that time permitted before the buses were ready for the return trip.

Numerous comments were made, and justly so, upon the excellence and adequacy of the arrangements for the entertainment of the guests and upon the simplicity and dignity of the dedication ceremonies.

tional and state problems of higher education.—*School and Society*

NINTH COLLOID SYMPOSIUM AT THE OHIO STATE UNIVERSITY

The Ninth Colloid Chemical Symposium of the American Chemical Society will be held in the Chemistry Building of The Ohio State University, on June 11, 12, and 13. PROFESSOR W. G. FRANCE, of the department of chemistry, is chairman of the local committee on arrangements.

The following papers will be presented:

"Optical Sensitizing in Photography," WILDER D. BANCROFT, J. W. ACKERMAN, and CATHERINE GALLAGHER, Cornell University.

"A Double Capillary Method for the Measurement of Interfacial Tension," F. E. BARTELL and G. L. MACK, University of Michigan.

"The Concentration of Ions at the Surface of Colloidal Clay Particles," RICHARD BRADFIELD, The Ohio State University.

"Bound Water," D. R. BRIGGS, Sprague Memorial Institute, University of Chicago.

"Studies on Electrokinetic Potentials. X. A Critical Study of Various Factors Influencing the Electrical Field of Force at Quartz-Aqueous Solution Interfaces," HENRY BULL and ROSS AIKEN GORTNER, University of Minnesota.

"The Coupled Nature of Lactic Acid-Glycogen Synthesis in Muscle," DEAN BURK, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

"The Composition of Soil Colloids in Relation to Soil Classification," HORACE G. BYERS and M. S. ANDERSON, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

"The Application of Colloid Chemistry in the Laboratory Diagnosis of Syphilis," HARRY EAGLE, The Johns Hopkins Hospital.

"A General Theory of Film Formation," C.W. FOULK, The Ohio State University.

"Precipitation of Proteins and Packing House Waste by Superchlorination," H. O. HALVERSON, University of Minnesota.

"Thickness of Interfacial Films and the Stability of Emulsions," W. D. HARKINS, University of Chicago.

"New Development in Cell Chemistry," TREAT B. JOHNSON, Yale University.

"Studies on Free and Bound Water in Elastic and Non-Elastic Gels," IVAN D. JONES and ROSS AIKEN GORTNER, University of Minnesota.

"Expanded Aerogels," S. S. KISTLER, College of the Pacific and Stanford University.

"Adsorption of Cations from Aqueous Solution by Silica Gel," I. M. KOLTHOFF and VERNON STENGER, University of Minnesota.

"The Microtome Method for the Determination of the Absolute Amount of Adsorption in a Static Air-Water Interface," JAMES W. MCBAIN, CECIL W. HUMPHREYS, and CHARLES BACON, Stanford University.

"Colloidal Aggregation and Some of Its Manifestations with Living Cells," STUART MUDD, R. L. NUGENT, and L. T. BULLOCK, University of Pennsylvania.

"The Constitution and Particle-Size Relations of Colloidal Ferric Oxide," J. B. NICHOLS and ELMER O. KRAEMER, E. I. du Pont de Nemours and Co.

"Studies in Chronaxie," G. H. RICHTER, Cornell University.

"Irritability and Anesthesia in Plants," J. E. RUTZLER, JR., Cornell University.

"Adsorption of Some Organic Substances to Silver Bromide," S. E. SHEPPARD, R. H. LAMBERT, and R. L. KEENAN, Eastman Kodak Company.

"The Electrical Conduction of Fibrous Materials," ALFRED J. STAMM, Forest Products Laboratory, U. S. Department of Agriculture.

"Mineral Flotation," ARTHUR F. TAGGART, Columbia University.

"The Setting of Plaster of Paris" (with motion pictures), HARRY B. WEISER and F. B. MORELAND, The Rice Institute.

"Colloidal Phenomena in Gall Stones," HARRY B. WEISER and G. R. GRAY, The Rice Institute.

"The Structure of Rubber and Other

HOSTS AND GUESTS AT THE LUNCHEON TENDERED BY THE DIVISION OF CHEMICAL EDUCATION TO THE TEACHERS OF INDIANAPOLIS AND VICINITY AT THE RECENT MEETING OF THE AMERICAN CHEMICAL SOCIETY

Elastic Colloids," G. W. WHITBY, National Research Council of Canada.

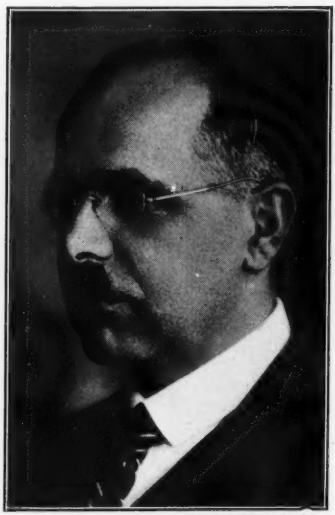
"Studies on Streaming Potentials of Capillaries of Various Sizes," HARVEY L. WHITE, FRANK URBAN, and E. T. KRICK, Washington University.

"The Colloid Chemistry of Electrical Insulating Materials," J. W. WILLIAMS, University of Wisconsin.

"The Kelly Tube and Sedimentation of Portland Cement," JAMES R. WITHROW and C. G. DUNCOMBE, The Ohio State University.

PROFESSOR FREUDENBERG TALKS UNDER TWO DOHME LECTURESHIPS AT HOPKINS

The seventh course of lectures on the Charles E. Dohme Memorial Lectureship was conducted at The Johns Hopkins University School of Hygiene and Public



The Nucleus

KARL FREUDENBERG

Health by PROFESSOR KARL FREUDENBERG, director of the Chemical Institute of the University of Heidelberg, and one of the foreign editors of the JOURNAL OF CHEMICAL EDUCATION. The lectures, which were given on April 16, 17, and 18, discussed Insulin, Optical Activity and Configuration of Oxy- and Amino-Acids, and Recent Researches on Cellulose and Starch.

The Charles E. Dohme Memorial Lectureship was established in June, 1916, by MRS. DOHME, the widow of a well-known pharmaceutical chemist of Baltimore, to promote the development of a more intimate relationship between chemistry, pharmacy, and medicine.

On April 17th, Professor Freudenberg also delivered a lecture on "Lignin" before the chemistry department of The Johns Hopkins University. This was held under the Dohme Foundation in connection with the National Fellowship Plan. This lectureship is maintained by DR. A. R. L. DOHME, of Baltimore.

POTASH CENTER MAY SHIFT TO ITALY

For generations the Stassfurt, Germany, beds of potash salts were the only large-scale sources of supply for the world. The trouble is not that potash does not occur elsewhere, but that it is found in combinations and concentrations that make its extraction a costly matter in competition with the German article. For instance, the volcanic rocks of Central Italy contain hundreds of thousands of tons of leucite, a mineral containing a silicate of aluminum and potash, but the extraction by the usual processes is not an economic proposition.

However, BARON GIAN ALBERTO BLANC, professor of geochemistry in the University of Rome, has just informed the British Institution of Chemical Engineers that his twelve years' study of this problem has borne fruit, and a large plant to treat 100 metric tons of leucite a day is nearly completed at Aurelia, near Rome.

Baron Blanc claims that his process requires only a very small amount of fuel, so that if large-scale working substantiates his experiments, Italy may have soon a prominent position in the world market for aluminum and potash salts.—*Science Service*

MERCK AND CO., INC., RENEWS ANALYTICAL FELLOWSHIP AT PRINCETON

The fellowship in analytical chemistry which Merck and Company, Inc., Rahway, N. J., established for the academic year 1930–1931 at Princeton University with an annual stipend of $1000 has been renewed for the year 1931–32. MR. I. C. SCHOONOVER, the first recipient, has also been awarded the fellowship for the coming academic year, and will continue the study of new potentiometric titration methods. Mr. Schoonover received his A.B. degree at George Washington University, and served two years as a junior chemist at the U. S. Bureau of Standards. He is one of the joint authors of a paper entitled "Two Hundred Reagent Chemicals Good and Bad," which was presented at the spring meeting of the A. C. S. at Indianapolis, Indiana.

INTERNATIONAL FELLOWSHIPS FOR RESEARCH

A list of international fellowships for research, compiled by the International Federation of University Women and published in pamphlet form, gives particulars of many hundreds of stipends available for advanced study and research in countries other than the stipendholder's own. The first and largest section relates to fellowships available only to nationals of one country. Among other interesting items in this section are forty-two American-German exchange scholarships and about one hundred seventy Hungarian scholarships tenable in Vienna, Rome, Berlin, Great Britain, and elsewhere. Great Britain's place in this section is a large one and so is Sweden's. Section II contains fellowships open to students from more than one country or irrespective of nationality. These are almost exclusively provided from British and American sources. Appended is a list of nineteen prizes open for international competition. Copies of the pamphlet can be obtained, price 1s. 3d. post free, from the British Federation of University Women, Crosby Hall, Cheyne Walk, London, S. W. 3.— *Nature*

COLD OF LIQUID HELIUM GIVES VERY CONDUCTIVE METALS

An extremely cold piece of tin conducts electricity a hundred thousand times better than tin at ordinary temperatures, it was confirmed by physicists of the National Bureau of Standards when they liquefied helium gas for the first time in the United States.

Helium is the most difficult gas to turn into liquid. A coil of tin through which electricity was passing was used by the scientists as one method of proving that they had achieved America's greatest cold, a temperature within three degrees Fahrenheit of the lowest temperature ever created by man. The greatest cold, called absolute zero, is 459 degrees below zero on the Fahrenheit scale. The lowest temperature reached in the Bureau of Standards experiment was minus 456 degrees Fahrenheit, while helium liquefied at minus 450 degrees.

DR. H. C. DICKINSON, DR. F. G. BRICKWEDDE, W. COOK, R. B. SCOTT, and J. M. SMOOT comprised the group that produced America's greatest cold. Working in constant danger of their lives, and late at night long after the other scientists had left Uncle Sam's great research laboratory, they won a friendly race with Johns Hopkins University and the University of California for the honor of being the first institution in America to liquefy helium.

Helium is the rare gas of the air, first discovered in the sun, which is obtained from natural gas in sufficient quantities to float in the air the giant airships of the American Navy.

To turn it from a gas into a liquid, the scientists first make liquid hydrogen by compressing this highly inflammable gas to 2200 pounds per square inch, cooling it with liquid air, then allowing it to expand in order to further cool itself. Then helium is compressed to 200 pounds per square inch and the liquid hydrogen is used to cool the helium. When the helium,

already intensely cold, is allowed to expand it gets so cold that it becomes liquid, the goal of the experiment.

Helium was first liquefied at Leiden, Holland, where the late PROFESSOR KAMMERLINGH ONNES pioneered in low-temperature research. The Berlin Imperial Institute and the University of Toronto have also made liquid helium.—*Science Service*

FLOUR FROM FISH MAKES HUMAN FOOD

A new product, fish flour, is about to be introduced to the palates of the American public through research by the U. S. Bureau of Fisheries and the U. S. Bureau of Chemistry and Soils. Valuable calcium, as well as many other essential minerals, is brought to the diet by this highly refined and biologically pure fish product. Fish meal has already found use to the extent of over a hundred thousand tons annually in this country as a crude food for animal feeding. The new fish flour is a preparation that will bring to the dinner table the same abundance of valuable mineral salts that has benefited animals to such a great extent.

The new flour is more highly refined than the animal fish meals and may in cooking be easily disguised to make the fish taste unrecognizable. At present the fish flour is not available commercially, but experiments by DR. J. A. LECLERC, of the Department of Agriculture's Cereals Laboratory, show that it can be used as a substitute for up to 15 per cent of white flour in sweet cookies.

Fish flour for human consumption is being produced experimentally by a commercial firm for the U. S. Bureau of Fisheries, by drying in vacuum the portions of fresh fish not now used commercially. When ground into a fine flour, it is white, fluffy, and attractive, with pleasant taste and odor.

Fish flour contains 25 to 30 per cent of mineral matter of which nearly half is lime. It also contains many other minerals, notably iodine which is valuable in the prevention and cure of simple goiter, and copper which has been found to be of aid in one type of nutritional anemia. Small amounts of other minerals contained in this preparation are vital to life although their functions are not fully recognized as yet. White wheat flour, for comparison, contains only a half of one per cent of mineral matter, of which less than one-twentieth is lime.

In baking cookies, fish flour can simply be substituted for some of the wheat flour, and no other deviation from any regular formula is necessary. The fish taste may be easily masked by the use of molasses, cinnamon, ginger, or other spices. Concealed by these flavorings, up to 15 per cent of fish flour may be substituted for ordinary white wheat flour without being detected.

Dr. LeClerc has figured that if three 10-gram cookies made with 10 per cent fish flour are eaten daily, in addition to the regular diet, by an individual who ordinarily takes two-thirds of a quart of milk a day, the calcium eaten will be increased by 20 per cent, which is sufficient to make the difference between a diet deficient or adequate in lime.—*Science Service*

ATOM NUCLEUS YIELDS SECRETS TO BOMBARDMENT

The mysterious inner core of the atom is probably built on the same lines as the outer shells, that is, like an uneven staircase. DRS. J. C. CHADWICK, J. E. R. CONSTABLE, and E. C. POLLARD, of the University of Cambridge, have bombarded a variety of atomic nuclei with fast-moving alpha rays from polonium, a radioactive element. They found that energy is done up in packets or quantized in the nucleus as elsewhere in the atom.

"What is happening in the inner core of the atom?" is the question that is being asked now in many laboratories of physics. The nature of the electron layers that form the bulky outer coat of the atom is well known but the very small nucleus which gives matter its weight is still a problem.

Protons, electrons, and alpha particles are the constituents of the nucleus, say these Cambridge scientists. The protons are themselves nuclei of the smallest atoms, that is of hydrogen, while the alpha particles are helium nuclei.

Protons have been ejected from certain atoms by Dr. Chadwick by bombarding them with the rapidly moving alpha particles from the polonium, an element very like radium. Two things may happen. The destructive alpha particle may be swallowed up by the second nucleus or it may escape again. In both cases Dr. Chadwick found proton rays were produced. If the alpha particle penetrates the target nucleus, protons of only two or three definite speeds are produced. Thus only limited and fixed amounts of energy can come from the nucleus at these times and fresh evidence is found for the quantum theory which has been so powerful in probing the structure of the atom.

Non-penetrating collisions, however, lead to protons whose speed depends on the speed of the guilty alpha particle. As might be expected, more of such protons are found along the line of motion of the hitting alpha particle than in other directions.

The proton speed groups have given the Cambridge scientists proof of the existence of energy levels in the nucleus, at least so far as the protons are concerned. Nothing is yet known about the behavior of the electrons in the nucleus.—*Science Service*

MAGNESIUM STARVATION FOUND TO CAUSE DEATH

A new kind of starvation due to lack of magnesium and a hitherto unsuspected relation between the adrenal glands of secretion and magnesium as a constituent of the diet was revealed for the first time recently by DR. E. V. MCCOLLUM and DR. ELSA ORENT of The Johns Hopkins School of Hygiene and Public Health, Baltimore. Their report was made at the meeting of the American Society of Biological Chemists. Convulsive death results from the magnesium lack.

Dr. McCollum, a pioneer in the study of vitamins, has thus demonstrated another essential to life itself. Magnesium is familiar as a metal, lighter in weight than aluminum. It also is a part of many chemicals. It is contained in the drugs, milk of magnesia, and Epsom salts. A very small amount of magnesium is a necessary part of the normal diet. How necessary it is and why has only just been disclosed.

Eleven days of a diet wholly lacking in this element causes convulsions and death in the majority of rats, Drs. McCollum and Orent found. On the third day of a magnesium-free diet white rats developed bright red ears and tails. In fact, wherever the skin showed through the hair, it was seen to be very red instead of the usual color. Apparently the outlying blood vessels were wide open so that all the blood flowed to the ends of the vessels just beneath the skin.

On about the tenth day of this diet, never later than the eleventh, the rats behaved very strangely. Ordinarily they pay no attention to what is going on about them and are undisturbed by noise. But after ten days of the diet, the slightest noise, such as the rattling of a piece of paper, or a shadow falling across the cage, agitated the rats so greatly that they whirled around two or three times and collapsed in a clonic spasm. Their breathing was disturbed, their eyes protruded, and at the same time the blood rushed away from the vessels just under the skin so that the ears and tails were blanched. The blood rushed to the heart, the small blood vessels contracted, and since the heart could not pump the blood out again it became enormously enlarged. Over four-fifths of the rats, 85 per cent of them, died in this spasm, the remaining 15 per cent lived on indefinitely, some for as long as 90 days, a long period in the life cycle of a rat.

When magnesium is omitted from the diet, calcium and phosphorus are drained out of the body, so that not enough is left to make an X-ray of the rat's skeleton.

This is the only way known to decalcify the body.

The explanation for all this, Dr. McCollum thinks, is that there is much the same relation between the adrenal glands and magnesium as there is between the thyroid gland and iodine, or the parathyroid glands and calcium. In the convulsions of parathyroid tetany, the nervous system can be quieted by administration of calcium. The symptoms of magnesium deprivation seem to be exaggerations of the adrenal glands' response to fear or anger.

Here is evidence that two more endocrine gland systems are tied up with two inorganic structures. No relation between them has been known before, Dr. McCollum pointed out, referring to the magnesium study and to his previous study on the effect of manganese on the body. Absence of this substance effects propagation and rearing of the young, even wiping out such a powerful emotion as maternal solicitude, he reported.—*Science Service*

CHEMICAL DEVELOPMENTS REPORTED AT THE INDIANAPOLIS MEETING OF THE A. C. S.

Cosmic Rays as Atom-Building Signals Questioned

Not enough atom-forming collisions occur in the depths of space to account for the intensity of penetrating cosmic radiation observed here on the earth, DR. L. S. KASSEL, of the U. S. Bureau of Mines at Pittsburgh, told the American Chemical Society.

The theory of DR. R. A. MILLIKAN and DR. G. H. CAMERON of the California Institute of Technology that atom-building is the cause of the ultra-X-radiation that streams down into the earth's atmosphere from above, would require that in the formation of an iron atom, for instance, 28 electrons and 56 protons or hydrogen atom cores would need to meet at the right time. Dr. Kassel asserted that collisions occur ten million billion times too seldom for this. His calculation, however, is based on the building of iron atoms, one of the many kinds of atoms which may give rise to penetrating rays, during their formation.

Auto Cylinder Gases Glow after Explosion

Photographs of individual explosions in a gasoline engine were shown by DR. LLOYD L. WITHROW and T. A. BOYD of the General Motors Research Laboratories. Much interest was caused by their report that "the products of combustion continue to emit light for some time" after the main burning process is over. Before this happens a narrow sheet of flame travels steadily through the charge and most of the burning takes place in this zone. The brightness of the afterglow increases with increasing pressure of the gases during the explosion. The method has been used to identify and study "knock" in auto engines.

Drugs Jelly Brain and Nerves

Coagulation or clotting of the liquid protein substances of brain and sensory nerves is the cause of the action of common anesthetic drugs. A challenge to the chemist is contained in this statement by PROFESSOR W. D. BANCROFT of Cornell University. Practically nothing is known about the nature or the properties of these animal proteins, said Dr. Bancroft.

Different proteins occur in different parts of the nervous system, for suitable drugs can cause jellying of one region while leaving others untouched. Veronal causes reversible coagulation of the brain proteins without affecting the sensory nerves. Histamine coagulates the proteins of the sensory nerves. Curare causes partial clotting of the motor nerves, while potassium salts affect the proteins of muscle.

Professor Bancroft's report was presented jointly by himself and DRS. J. H. RICHTER and J. E. RUTZLER, also of Cornell University.

Better Anesthetics Result from Chemical Research

More effective sleep-producing and anesthetic drugs have been produced

through research by DR. H. A. SHONLE of the Lilly Research Laboratories, Indianapolis, Ind.

The possibility of predicting the duration and the effectiveness of hypnotic sleep-producing drugs that have not yet been synthesized by the chemist is stressed in a report to the A. C. S.

Through the use of a new group of anesthetics, known as the amyl ethyl barbituric acids, developed by Dr. Shonle and his associates, it is possible for physicians to reduce the nausea that often follows operations, give the patients greater comfort and subject them to far less mental distress.

These amyl ethyl barbituric acids will not replace ether and other major anesthetics but they find use as substitutes for morphine in making the patient ready for the unpleasant experience of an operation. Since the new compounds are not habit-forming like morphine and other opium preparations, there is no danger of causing drug addicts through their use.

The new drugs are closely related to veronal, or barbital, a synthetic compound that has found use in medicine as a sleep-producing drug. Alcohol, which Dr. Shonle calles the "simplest hypnotic," is one of the constitutional parents of the new anesthetics. Part of the alcohol molecule is replaced with barbituric acid, then a part of the barbituric acid is replaced with what chemists know as an amyl group. This makes the anesthetic action more rapid and the patient recovers faster. If plain alcohol were used, fifty times the dose of barbituric acid would be necessary to produce the same hypnotic effect. Veronal is a barbituric acid with two groups of ethyl in its structure instead of the one ethyl and one amyl in the new compounds.

Radium May Be Used in Vitamin Production

Possibility of radium playing a rôle in vitamin production, at least in the laboratory, appeared when PROFESSOR THOMAS DEVRIES of Purdue University announced that he and his former colleague, the late PROFESSOR RICHARD B. MOORE, had succeeded in activating ergosterol by radium rays. Activated ergosterol is a potent source of vitamin D, it has been shown by PROFESSOR HARRY STEENBOCK of the University of Wisconsin. The Steenbock method, which has been patented, activates the ergosterol by ultra-violet rays.

The radium-activated ergosterol reached a degree of potency equal to one thousand times that of a good grade of cod-liver oil or one-hundreth of that obtained by the Steenbock ultra-violet ray method, Proffessor De Vries reported. "Radium-activated ergosterol is not yet commercially feasible," he said in reply to a *Science Service* inquiry. Patents are now pending on this method.

Electrons and Protons Paired in Atom Nucleus

Atoms whose weight-bearing cores contain even numbers of both electrons and protons are twenty times more frequent than all others, PROFESSOR WILLIAM D. HARKINS, of the University of Chicago, reported. Of all the chemical elements found on the earth, said Professor Harkins, 95 per cent belong to a class in which each building stone of the atomic core has a mate. The electrons of a pair in the central heart of the atom are not absolutely identical, however. One is spinning in the opposite sense to the other. Thus the nucleus as a whole is free from spin.

These facts throw very important light on the stability of atoms and therefore on the reason why some chemical elements, like radium, are continuously disintegrating into simpler atoms.—*Science Service*

PART OF COSMIC RAYS MAY COME FROM SUN

Cosmic rays, the intensely "hard," all-pervading radiation that comes from somewhere in outer space, may come in some small degree from the sun. This is indicated by recent researches of PROFESSOR VIKTOR HESS of the University of Graz, one of the pioneers of cosmic ray research.

With instruments set on heights in the Alps, he and other physicists have detected a very slight increase in the intensity of the radiation when the sun is at mid-heaven. This averages only about one-half of one per cent of the total radiation, but according to Professor Hess it is a constant, and hence probably significant, variation.

If the sun really is the source of even a small fraction of the cosmic radiation, it lends support to the view held by a number of European scientists, that these rays come from the stars, for the sun itself is a star, and not a very large one at that. Experiments conducted by two of Professor Hess' colleagues, DR. O. MATHIAS and DR. STEINMAURER, have indicated that there is about a two per cent daily variation from average intensity. They are still engaged in checking up on this result.

Professor Hess adds, however, that even if the stars are definitely shown to be sources of cosmic rays, this does not wholly shut out the possibility of a part of the rays coming also from interstellar space, the source believed in by the American school of investigators.—*Science Service*

KNIFE-MARKED CHINA INVESTIGATED BY SCIENTISTS

Why does cutlery sometimes leave unsightly marks on china which cannot be removed by washing? Scientists at the U. S. Bureau of Standards are investigating the question, following complaints that the stroke of cutting even a tender piece of meat on a plate or platter is often sufficient to scar the housewife's dishes permanently with pencil-like markings.

Some factor in the baking process of china may account for the fact that some pieces appear immune to cutlery markings, while others are readily discolored, the preliminary findings show. An excess of carbon in the furnace did not appear to make the dishes susceptible to marking but sulfur dioxide gas in the furnace did make the china more liable to scratching with metal, particularly with nickel and steel.

Dishes just removed from the oven and not washed after baking marked readily, as did glass surfaces that had been dried by heating at temperatures above 400 degrees Centigrade. When the glass surface retained some moisture to act as a lubricating film, the marking did not occur.—*Science Service*

MUSIC OF ALCOHOL ON RADIO

Alcohol was on the air when DR. DONALD H. ANDREWS of Johns Hopkins University recently played the hidden music of this and other chemical substances in a *Science Service* radio talk over the nation-wide network of the Columbia Broadcasting System. The music of the spheres, which up till now existed entirely in the poet's imagination, said Dr. Andrews, is being approached in a tangible way by recent developments in science and indeed was actually transposed and played by him as chords and runs on the piano in the course of his talk.

SIR CHANDRASEKHARA V. RAMAN of Calcutta, India, has recently given physicists a new way of listening to, or really seeing, the music of the atoms. The Raman spectrum, said Dr. Andrews, shows us that a molecule, such as one unit of water, is really a little musical instrument, much like a harp, playing its own characteristic tune.

"Of course you do not hear it if you hold a glass of water up to your ear because the tune is pitched many millions of times higher than the highest note on a piano or violin," Dr. Andrews said. "In fact, it is really light and not sound that is given off. By photographing this light, however, we can detect the notes that are present, and can transpose them to a lower frequency just as you shift a chord from the top to the bottom of the piano. In this way the atomic music can be brought down to a range where we can hear it, and play it on any familiar instrument."

The chords of water, grain alcohol, wood

alcohol, chloroform, benzene, gasoline, sulfuric acid were played in turn by Dr. Andrews. Alcohol had rather a sweet-sounding chord, but chloroform, like wood alcohol, was harsh. Gasoline gave a very modernistic chord extending over the entire range of the keyboard. Benzene was rather melancholy. Sulfuric acid was also very modern. The spectra or chords of several hundred different chemical compounds have been photographed and analyzed.

These experiments also provide much new material for musicians if they care to use it. Dr. Andrews closed his talk by playing a piece composed by ABRAM MOSES, formerly of the Peabody Institute of Music, in Baltimore. The composition was based on the chords of water, grain alcohol, and wood alcohol.—*Science Service*

DR. MENDENHALL DESCRIBES CHANGES IN BEHAVIOR OF FREE ELECTRONS

Science now believes that the electrons in a piece of cold metal are more active and sociable than formerly but current theories make it still as difficult for an electron to get a passport to the foreign air beyond the metal's boundaries.

DR. CHARLES E. MENDENHALL of the University of Wisconsin has presented to physicists an interesting picture of the changes in the behavior of the free or roaming electrons in metals, which has been brought about by the revolutionary discoveries of the new quantum theory. It is to the electrons of this kind that the most characteristic properties of metals are due, notably their reflecting surface and the ease with which they conduct electricity and heat.

Formerly there was no check on the activities of the individual electrons of this family. They were all vagrants. The new statistical theories of HEISENBERG, SCHRÖDINGER, and DIRAC change all this. Each electron is now registered in the census of the mathematical physicist, by a series of tags known as "quantum numbers."

Further, an edict known as Pauli's principle now decrees that a given series of number tags can belong to, at most, only two electrons. We can regard this series of numbers as the address of the electron in the phantom city of the physicist's imagination. Dr. Mendenhall describes this principle as "social legislation to prevent overcrowding of the electrons," an admirable contribution to electron welfare. . . . .

There are two ways in which the electrons can escape from their neatly arranged homes in the metal! 1. By the action of heat. 2. By the falling of a beam of light on the surface. It is with light that Dr. Mendenhall's experiments have been concerned. This so-called photo-electric effect has played a very important part in reviving SIR ISAAC NEWTON'S idea that light consists of particles rather than waves.

Only a few electrons, those that have much more energy than the rest, have the privilege of escaping from the metal when the artificial sun of the experimenter comes out. A wall of force known as the "work function" keeps all but a few within the city limits.

The changes introduced by the new theory of metals, due to PROFESSOR ARNOLD SOMMERFELD, might be compared to the effects of the industrial revolution. The average energy, or wealth, of the floating electron population is now believed to be much higher than formerly. It is this energy that enables an electron to get around and do things and to escape from the metal from time to time.

Professor Sommerfeld seems at first to have done an excellent thing. It turns out, however, that the disobliging wall of force has increased under the new régime to just the same degree as the average energy, and it is just as troublesome as before for an ambitious electron to break through the surface of the metal and cavort before the waiting experimenter.

Dr. Mendenhall says this is a "protectionist trick by which wages are increased but prices go up correspondingly." These

effects, however, influence the electrons on the surface, that is in the first thousand or ten thousand layers of atoms. Dr. Mendenhall's recent experiments have helped check the application to metals of this new quantum theory, which scientists believe is of much more immediate importance than Einstein's relativity theory.—*Science Service*

NEW DRUG RELIEVES PAIN OF LEAD COLIC, GALLSTONE COLIC

The intense pain of lead colic, gallstone colic, and ureteral colic can be relieved by slow injection into the vein of calcium chloride, a salt of the metal which is necessary for bone formation, DRS. WALTER BAUER, WILLIAM T. SALTER, and JOSEPH C. AUB of the Massachusetts General Hospital, Boston, have just found. This gives more rapid relief than any other form of treatment tried by these physicians. Their discovery of this new use of a calcium salt and of a way to give relief in these distressing conditions was made in the course of studies on the treatment of lead poisoning, they stated in their report to the American Medical Association.

Lead and calcium, they knew, were both retained in the body in the bones. The chemical behavior of certain lead and calcium salts in the body are very similar. These facts suggested to Dr. Aub that the same physiologic variations which influenced the elimination and excretion of calcium would similarly influence the lead stream.

Medicines that caused decalcification, or removal of calcium from the body, resulted in an increased excretion of lead, it was found. Conversely, treatment that increased calcium storage also increased storage of lead. Consequently in treating lead poisoning, a high calcium diet is used until all symptoms of the poisoning have disappeared, usually within one or two days. The theory underlying this is that following increased calcium retention as a result of the high-calcium diet, the lead is removed from the blood and stored in the bones. In order to hasten this process and give more prompt relief from the severe pain of lead colic, Dr. Aub and associates tried giving a solution of calcium chloride directly into the veins.

The results were dramatic, they reported. The pain stopped almost immediately, often before the injection was completed. Such prompt relief made them doubt whether the beneficial action of the calcium salt was due to fixation of lead and calcium salt in the bones. Further studies indicated that the calcium salt acts as an antispasmodic. The mechanism of its action, however, remains unexplained at present.—*Science Service*

FIND WAY TO ELIMINATE DANGER IN SERUM TREATMENT

A new chemical process that is expected to eliminate all danger from protective or curative serum administrations was reported by PROFESSOR J. BRONFENBRENNER of Washington University, St. Louis, at the Cleveland meeting of the American Association of Immunologists in April. The use of these sera has become increasingly popular for treating diseases and for giving protection from diseases. Toxin-antitoxin for diphtheria and antitetany injections are familiar examples. Occasionally, however, such serum injections are followed by grave complications and even death. This has made some physicians hesitate to use the sera.

Only one in 20,000 of those receiving serum for the first time develop alarming symptoms and only one in 50,000 die as a direct result of the treatment. Medical scientists are trying now to eliminate this last bit of hazard. The reason for the hazard is that some persons have a specific sensitivity to foreign protein. Such are the victims of asthma and hay fever. The same protein does not always affect all sensitive individuals, some being sensitive to the protein of horse serum, and not sensitive to serum from other animals or to protein from other sources. The human race may be divided into four categories

with respect to their response to injections of these sera, Professor Bronfenbrenner pointed out. Some, about one-tenth, have no ill effects after the injections. A small group, about one in 20,000, respond to injection of horse serum by an immediate violent reaction leading to collapse and sometimes death.

The bulk of people when given serum injections have so-called serum sickness to more or less severe degree, varying from soreness at the point of injection to generalized fever and indisposition. These are considered normal in their reactions, however. The fourth group is composed of persons who may have reacted normally originally, but who became sensitive to serum as a result of previous injection. These may develop serum sickness very quickly and some of them may suffer severe complications and even die.

The process developed by Professor Bronfenbrenner and his colleagues, D. M. HETLER and I. O. EAGLE of Washington University, changes the chemical nature of the serum protein, so that it loses the quality of causing a specific reaction to it, but at the same time the immunizing or curative properties of the serum are left almost as effective as they were in the original serum. Studies with animals showed that the new preparation of sera were not toxic. Further improvement of the chemical procedures is being sought in order to leave the curative and immunizing properties of the sera unaffected in potency.—*Science Service*

SECOND INTERNATIONAL CONGRESS OF THE HISTORY OF SCIENCE AND TECHNOLOGY

The Second International Congress of the History of Science and Technology will be held in London, June 29–July 3, under the presidency of DR. CHARLES SINGER.

The Congress originated with the Comité International d'Histoire des Sciences which was founded at Oslo on August 17, 1928. This body meets annually in Paris and organizes every three years a Congress in which persons interested in the History of Science and Technology are invited to take part. For the coming Congress the Comité International des Sciences Historiques, the History of Science Society, Washington, D. C., and the Newcomen Society for the Study of the History of Engineering and Technology, London, will coöperate.

Papers and discussions at this year's meeting will center around the sciences as an integral part of general historical study, historical and contemporary inter-relationship of the physical and biological sciences, and the interdependence of pure and applied science.

Receptions have been arranged at the Royal Society, the Royal Society of Medicine, the Royal Institution of Great Britain, the Royal College of Physicians, the Royal Observatory, Greenwich, the Royal Botanic Gardens, Kew, the Science Museum, the Natural History Museum, the National Portrait Gallery, the Institute of Historical Research, Barbers Hall, and Down House, Kent.

A special exhibition of manuscripts and early printed books illustrative of the history of science and technology will be assembled at the British Museum and will be open to members of the Congress throughout the week. An exhibition of modern publications on the history of science and technology will be arranged for the Congress at the Science Museum.

The headquarters will be the Science Museum, South Kensington, London, S. W. 7, and all communications should be addressed to the Secretary there.

DR. VON WEIMARN HONORED IN OSAKA

On February 15 the Osaka Industrial Research Institute of the Commerce Office honored DR. P. P. VON WEIMARN on the occasion of the twenty-fifth anniversary of his discovery of the Law of Universality of the Colloid State of Matter. Dr. von Weimarn is a consulting engineer of the Institute. He has been a resident of Japan since 1921, when he left Russia, his native country, on account of the revolution. He

has lectured at the Universities of Tokyo, Tohoku, and Kyoto, and before receiving his present appointment, directed research in colloid chemistry in the chemico-physical seminary of the Kyoto Imperial University for five years.

Dr. von Weimarn was born in St. Petersburg on July 18, 1879, the eldest son of a general under the Tsarist régime. He attended the Catherine II University of Mining. He taught for some years in his alma mater and in 1919 became president of the Technical University of Vladivostok.

His discovery of the Law of the Universality of the Colloid State of Matter in 1906 has been recognized by awards from a number of scientific academies.

SCIENCE HEADQUARTERS MAY OVERSHADOW WESTMINSTER ABBEY

Westminster Abbey, perhaps London's most famous and historic building, may soon have an ultra-modern neighbor if plans to concentrate scientific societies mature. The leading scientific and technical associations of Britain, now federated under the title of the Association of Scientific and Technical Associations, Inc., have secured an option on a near-by site, and contemplate erecting a building to house all the constituent bodies. It is hoped also that certain kindred institutions and national associations representing the commercial side of the various industries concerned will take advantage of the accommodation.

The plans provide for a distinct "Chemical Wing" to house the Chemical Society, the Society of Chemical Industry, the Institute of Chemistry, and other similar organizations, which will occupy two-fifths of the proposed building, and be a self-contained vertical section through the whole seven floors.

A capital sum of at least $1,750,000 will be required, the cost of upkeep being expected to be met by rents received from the tenant institutions.—*Science Service*

CHEMICAL BOOKS OF HISTORIC INTEREST FOUND IN BODLEIAN LIBRARY

The following is quoted from *Nature:*

A chemical library of historic interest has just been discovered in the Bodleian Library by DR. R. T. GUNTHER, who has published a list of twenty-three of the books in the recent issue of the *Bodleian Quarterly Record*. The greater number of volumes now described were given, in 1683, by various benefactors to form the nucleus of a departmental library when the Ashmolean Chemical Laboratory was opened, as described in *Nature* for April 2, 1927. The existence of this venerable collection of books, the oldest chemical library in Britain, had long been forgotten owing to loss and dispersal of its volumes to fill gaps in the series of Ashmolean manuscripts, with which it had nothing to do. Fortunately, the names of donors have been inscribed in several of the books, thus establishing their identity. The more important gifts came from the vice-chancellor, the dean and other members of

Christ Church, from Dr. Plot, the first professor of chemistry, and from John Cross, the "privileged" apothecary at whose premises, in the Oxford High Street, Boyle and Hooke conducted their epoch-making researches in "pneumaticks." None of the books is recorded as having been presented by Ashmole, although he was the founder of the professorship of chemistry.

A notice in *Chemistry and Industry* states that the recently discovered library includes copies of Libavius, Paracelsus, Agricola, Beguin, Boyle, Becher, Lémery, and others.

VISITING PROFESSORS TO TEACH IN SUMMER SCHOOL OF THE OHIO STATE UNIVERSITY

PROFESSOR H. B. WEISER, of Rice Institute, will be in teaching residence in the department of chemistry of The Ohio State University for the Summer Quarter. DR. R. C. FUSON of the University of Illinois and DR. M. G. MELLON of Purdue University will also augment the summer staff in chemistry. Professor Mellon will present historical, biographical, and inorganic chemistry, while Professor Fuson will teach organic chemistry.

MALTBIE CHEMICAL COMPANY CONTINUES RESEARCH FELLOWSHIP AT PHILADELPHIA COLLEGE OF PHARMACY

The Maltbie Chemical Company of Newark, New Jersey, has instituted a research fellowship at the Philadelphia College of Pharmacy and Science to continue the work already done under a fellowship granted by the same firm last year. The subject of these investigations at the Philadelphia College is the germicidal value and toxicity of creosote and its fractions.

The work began March 1 and will continue until July 1. The holder of the fellowship is RALPH PRESSMAN, 1929 graduate of the Philadelphia College, who was the holder of the fellowship last year. The work is under the supervision of DR. HORATIO C. WOOD, JR., professor of materia medica, and DR. LOUIS GERSHENFELD, professor of bacteriology and hygiene.

SIOUX VALLEY CHEMISTS CLUB MEETS

The Sioux Valley Chemists Club held its third meeting of the year at Vermilion, South Dakota, March 28. The following papers were read: "The Oxygen Compounds of Fluorine," by DR. GEORGE H. CADY, professor of physical chemistry of the University of South Dakota; "Permeability of the Blood Cells," by ALFRED J. BENESH, graduate student of the biochemistry department; "Biography of Harvey W. Wiley," by GUY G. FRARY, state chemist.

PROFESSORS DAVIS AND CLEAVELAND TO LECTURE AT WESTERN RESERVE SUMMER SESSION

PROFESSOR TENNEY L. DAVIS of the Massachusetts Institute of Technology, will be the special lecturer in organic chemistry for the forthcoming summer session of Western Reserve University. Professor Davis will offer two courses of lectures; the first, a course on the Mechanism of Organic Reactions, in which he will emphasize particularly the modern theories including the latest developments on the nitrogen derivatives which are his own particular interest; the second, a course on the history of chemistry, showing the rise and development of modern chemistry.

PROFESSOR MARION CLEAVELAND will offer a new course on Chemical Conversions by Means of Micro-organisms, consisting of lectures dealing with important chemical changes brought about through the agency of bacteria, yeasts, and molds. This is offered because of the rapidly increasing importance of fermentation processes in industry.

DR. McMASTER COMPLETES TWENTY-FIVE YEARS AT WASHINGTON UNIVERSITY

DR. LEROY MCMASTER will complete twenty-five years of service as a teacher of chemistry in Washington University, St. Louis, Missouri, in June. For the past nineteen years he has been head of the department of chemistry. On April 11, a large number of his present and former students and colleagues met at the University Club for a testimonial dinner in his honor. PROFESSOR WALTER E. MCCOURT, assistant chancellor of the university, who is also completing twenty-five years, presided. The felicitations of the university were expressed by CHANCELLOR GEORGE R. THROOP. PROFESSOR RALPH SHRINER of the University of Illinois spoke on behalf of the alumni and paid high tribute to the guest of honor as a chemist and teacher. MR. CHARLES NAYLOR, a student in the graduate school, represented the present students and PROFESSOR T. R. BALL acted as spokesman for the faculty of the department of chemistry.

THE DISTRICT OF COLUMBIA ASSOCIATION OF CHEMISTRY TEACHERS MEETS

The 1931 meeting of the District of Columbia Association of Chemistry Teachers was held in the chemistry lecture room of Central High School in Washington, on the evening of April 16.

PRESIDENT J. A. MULDOON called the meeting to order. The first speaker of the evening was DEAN HARDEE CHAMBLISS of the Catholic University of America who spoke on the construction and operation of the government's nitrate plant at Muscle Shoals. Dr. Chambliss served as commanding officer of the plant during the World War and as superintendent for several years after the war. He presented a survey of the operations of the plant.

Following Dr. Chambliss' address, DR. LEWIS WARREN, of the Department of Agriculture, Bureau of Chemistry, discussed the constitution of various drugs. In closing he particularly emphasized the nation's need for industrial chemists, stating that "there are needed now about five chemists for every one that is employed today."

The following officers were then elected for the ensuing year: *President*, HENRY P. WARD, Catholic University of America; *Sec.-Treas.*, CHAS. E. BISH, Western High School; *Senators*, REV. GEO. L. COYLE, Georgetown University; ALLEN J. MARSH, McKinley High School; MR. SMITH, Central High School.

INSTITUTE OF METALS WILL MEET IN SWITZERLAND

Switzerland will be the scene of this year's autumn meeting of the Institute of Metals. It will be held in Zürich from September 13–18 by invitation of the Schweizerische verband für Materialprüfung. The evening of September 13 will be devoted to the formal opening of the meeting, addresses of welcome by the inviting body and the Autumn Lecture. The latter is to be given by MR. U. R. EVANS, on "Thin Films on Metals in Relation to Corrosion Problems." After the lecture an entertainment will be given in the Great Hall of the Zürich Polytechnic.

The mornings of September 14 and 15 will be devoted to the reading and discussion of papers, while for the afternoons, visits have been provisionally arranged to the works of Messrs. Escher, Wyss & Co., Zürich; Maschinenfabrik Oerlikon, Oerlikon; Messrs. Brown, Boveri & Co., Baden; Messrs. Sulzer Brothers, Winterthur; Kraftwerke Wäggital, Wäggital; Messrs. Eisen & Stahlwerke vorm. G. Fischer, Schaffhausen; and Messrs. Alfred J. Amsler & Co., Schaffhausen.

A Ladies Committee is arranging visits by the ladies of the party to the Kunsthaus, Uetliberg, Landesmuseum, and the Wäggital. In the evening of September 14 members and their ladies will be the guests of the city and canton of Zürich at one of the hotels on the heights above the city, while for the next evening an excur-

sion by steamer on Lake Zürich, followed by a dinner and dance at a lake-side village, is being arranged.

On September 16 an excursion will take place to the Rigi, the party going thence by steamer to Lucerne, where the night will be spent.

On September 18 the main party will divide, one going to Biel to visit a watch factory and leaving for England in the evening, while the other will go via Lötschberg to visit the new aluminum alloys rolling mills at Chippis-Siders in the Rhône Valley. From Chippis members will either return to London via Lausanne or Geneva, or proceed via the Simplon to Milan to take part in the International Foundry Exhibition and Congress, which continues at Milan until September 27.

During the week preceding the Institute of Metals Meeting there will be held, also in Zürich, the first congress of the New International Association for Testing Materials; thus, inclusive of the Milan Congress, there will be taking place in Switzerland and Italy during September a series of meetings covering three weeks. In view of the fortunate juxtaposition of these important international gatherings, it is expected that they will be largely attended by metallurgists and engineers from all parts of the world.

Further particulars may be obtained on application to MR. G. SHAW SCOTT, 36–38 Victoria Street, London, S. W. 1.

DEUTSCHE BUNSEN GESELLSCHAFT

The following papers have been added to the program of the meeting of the German Bunsen Society for applied physical chemistry, which will take place in Vienna, May 25–28: "Technical Advances in the Sphere of Electro-Chemistry," J. BILLITTER, Vienna; "The Time Law of Transformation of Deformed Metal," F. SAUERWALD, Breslau; "Di-Pole Moments of Inorganic Compounds," H. ULRICH, Rostock; "Cinematographic Representation of the Recrystallization of Rock Salt," K. PRZIBAM, Vienna; "Electrolytic-Chromium Plating of Light Metals," A. KOENIG, Karlsruhe; "The Formation of Sulfide Layers on Silver Considered with Regard to Oxidation of Metals," K. FISCHBECK, Tübingen; "The Technology and Applications of Electron Metal," W. SCHMIDT, Bitterfeld; "Electrically Prepared Oxide Films in Aluminum," H. RÖHRIG, Lautawerk.

INTERCOLLEGIATE STUDENT SCIENTIFIC CONFERENCE AT MOUNT HOLYOKE

On April 11, at Mount Holyoke College, there was held an Intercollegiate Student Scientific Conference which is the first of its kind and from that point of view is of scientific interest. The idea of the conference originated with the scientific students at Mount Holyoke last year, and they had an interdepartmental meeting at that time. This year they invited the neighboring Connecticut Valley colleges to participate and to make it an intercollegiate conference. The colleges which actively participated were Connecticut College for Women, Massachusetts State College, Mount Holyoke College, Springfield College, Smith College, and Wesleyan University. The organization and planning was done largely by the students and the interest they have shown has been quite remarkable. The reports and the demonstrations were largely given by undergraduates, a few being done by graduate students. The registration of students from colleges other than Mount Holyoke was one hundred sixty-two.

Following the opening meeting the day was given over to sectional meetings and demonstrations in the ten sciences—anthropology, astronomy, botany, chemistry, geology, physics, physiology, psychology, mathematics, and zoölogy—with the exception of an hour's interlude for luncheon in the Wilbur Banquet Hall and a concluding general lecture by PROFESSOR FREDERICK A. SAUNDERS, of the department of physics at Harvard University, who spoke on "Every Man's Atom," at which there was an attendance of over three hundred.

Exhibits, reports, and demonstrations went on simultaneously in all parts of Clapp Laboratory, Shattuck Hall, and Williston Observatory. The most interesting and unusual demonstrations were repeated several times during the day in order to make it possible for most of the delegates to see them.

It is hoped that following the present conference some permanent organization will be devised whereby the conference shall meet regularly at a different college each year, and shall expand its size so as to be comparable in its scope to the model assembly of the League of Nations.

ENGINEERS' DAY AT WASHINGTON UNIVERSITY

The students of the schools of engineering and architecture of Washington University, Saint Louis, Missouri, celebrated Engineers' Day on March 20. The division of chemical engineering held open house at Busch Hall, the chemistry building, and in a variety of exhibits justified its classification as one of the established branches of engineering.

The chemical engineering laboratory emphasized the strictly engineering phases of the subject. The uses of various types of filtration machines, a column still, a supercentrifuge, a hydrogenation outfit, a steam kettle, and electric flow meters were demonstrated. The analysis of fuel gas and its engineering significance was pointed out. Rustproofing of iron and steel by means of an electrodeposited alloy drew the largest crowds of any exhibits in this room. This zinc-cadmium alloy and its method of application has been developed in this laboratory.

Liquid-air experiments were performed a number of times during the day before capacity crowds in the main lecture room. MR. CHARLES L. FAUST presented the demonstrated lecture.

To emphasize the chemical background necessary for the chemical engineer the following exhibits were provided:

The analytical laboratory showed the analysis of steel, fat extractions, electrolytic, and electrometric determinations, and, of general interest, the analysis of "hootch." A popular demonstrated talk on radium drew large crowds.

The organic laboratory had exhibits showing the laboratory operations of crystallization, sublimation, and distillation. Laboratory preparation of chloroform, formaldehyde, aspirin, soap, and amyl acetate interested numbers of chemically minded individuals. A glass blowing demonstration proved a "drawing card" for this laboratory.

The physical chemistry laboratory had exhibits of colloids. Spectroscopic and photometric demonstrations of neon signs also proved to be an attraction.

The usual displays of chemical magic caused the "profane" to marvel at the powers of chemistry.

The building was crowded until late. Many of the visitors were persons connected with the various schools of the university. However, the engineers were gratified at the large attendance of the citizens from the metropolitan Saint Louis, who have no direct connection with the institution. In this way Engineers' Day served to stress the importance of engineering education at Washington University.

The students in chemical engineering were particularly glad to welcome DR. W. F. BROWN and a few of his senior students in chemical engineering from Kansas State A. and M. College. Dr. Brown and his students were in Saint Louis on their annual inspection trip and naturally came out to look things over. Due to the fact that their celebration of Engineers' Day had come the week before, they were sympathetic visitors.

Engineers' Day festivities ended with the Engineers' Masque on Saturday night, March 21. The gymnasium of the woman's building was decorated in an artistic manner and the dance was a most enjoyable affair.

UNIVERSITY OF MARYLAND FOURTH BIENNIAL CHEM SHO

The fourth biennial Chem Sho, under the direction of Alpha Chi Sigma Fra-

ternity, was held at the University of Maryland on April the 22nd. This consisted chiefly of a liquid air demonstration and Einstein's moving picture film on relativity.

Among the exhibits that attracted attention were the following: dust explosions, rubber plating, spinthariscopes, smoke rings, spectroscope, time reactions, plastics and molded products, the working unit of an electrolux refrigerator, everflow spigot, model of synthetic ammonia plant, phytochemical and plant pigments, copper plating, gas coulometers, Brownian movement, molecular movement, Geissler tubes, exhibits of industrial products, mineral specimens, odors, ozonizer, stereoptican slides on snow crystals, and ever-moving moth balls.

DR. BUEHLER ADDRESSES THE IRA REMSEN SOCIETY OF THE MISSOURI SCHOOL OF MINES

DR. H. A. BUEHLER, chief of the Missouri Bureau of Geology and Mines, was the speaker of the evening at the March 4th meeting of the Ira Remsen Society at the School of Mines and Metallurgy of the University of Missouri.

Dr. Buehler stated that the study of geology is based upon chemistry, and that one would not get far in fundamental geology unless he has a thorough knowledge of chemistry. There is no process of any consequence that cannot be traced to a chemical basis. Dr. Buehler outlined the geology of the state of Missouri, with particular reference to the ore deposits, and discussed some of the chemical possibilities as to how these deposits occurred. He also outlined numerous problems yet to be solved in the study of geological formations, all having a direct chemical relation to their solution.

A part of Dr. Buehler's talk dealt with chemical research in the Bureau of Geology and Mines, and especially the chemical study of drill cuttings and the residues from the chemical decomposition of these cuttings. The study and classification of these residues has made it possible to identify with remarkable accuracy the various geological formations penetrated in drilling.

WINNERS OF 1930-31 PRIZE ESSAY CONTEST FOR COLLEGES, AND NORMAL SCHOOLS AND STATE TEACHERS' COLLEGES*

College Contest

The Relation of Chemistry to Health and Disease

MARCEL GERARD EYE	The Ohio State University, Columbus, O.	Chemistry an as Aid to Public Health	(1)
VIRGINIA MARIE KENNARD	College of St. Mary-of-the-Wasatch, Salt Lake City, Utah	Synthetic Medicine	(2)
JOSEPH DAUBER	Massachusetts Institute of Technology, Cambridge, Mass.	Chemistry as an Aid to Public Health	(3)

The Relation of Chemistry to the Enrichment of Life

IMOGENE MARIE AARON	Mount St. Scholastica College, Atchison, Kansas	The Rôle of Chemistry in the Diffusion of Knowledge	(1)

* National high-school awards have not yet been made.

KATHERINE LOUISE WEBER	College of Wooster, Wooster, Ohio	How Chemistry Has Enriched Life in the Last Twenty-Five Years	(2)
MARGARET ELIZABETH MEYER	University of Denver, Denver, Colo.	How Chemistry Has Enriched Life in the Last Twenty-Five Years	(3)

The Relation of Chemistry to Agriculture or to Forestry

J. REID SHELTON	State University of Iowa, Iowa City, Iowa	The Industrial Utilization of Cornstalks and Corncobs	(1)
BETTY GRAY	Goucher College, Baltimore, Md.	The Utilization of By-Products in Agriculture	(2)
ALFRED ANDRE HOFFMAN	The University of Rochester, Rochester, N. Y.	Chemistry and the Utilization of Waste Products in Agriculture and Forestry	(3)

The Relation of Chemistry to National Defense

BRYCE L. CRAWFORD, JR.	Leland Stanford Junior University, Stanford University, Calif.	Chemistry and Aviation	(1)
HELEN FRANCIS LYONS	College of St. Mary-of-the - Wasatch, Salt Lake City, Utah	Chemical Warfare— Offensive and Defensive	(2)
CHARLOTTE BRADSHAW	College of St. Catherine, St. Paul, Minn.	Chemical Warfare— Offensive and Defensive	(3)

The Relation of Chemistry to the Home

DOROTHY MCCANNE	Goucher College, Baltimore, Md.	Chemistry and Better Food	(1)
ROGER BARRON MORRISON	Cornell University, Ithaca, N. Y.	Chemistry and Better Food	(2)
VIRGINIA RICHARDSON	MacMurray College, Jacksonville, Ill.	Sanitation	(3)

The Relation of Chemistry to the Development of an Industry or a Resource of the United States

WILLIAM R. MILLER	Fenn College, Cleveland, Ohio	The Relation of Chemistry to the Development of the Cellulose Industry	(1)
JOHN LELAND GARRISON	Duke University, Durham, N. C.	The Relationship of Chemistry to the Aluminum Industry	(2)
ALEX W. FRANCIS, JR.	Oklahoma A. & M. College, Stillwater, Okla.	The Utilization of a Resource in a Major Chemical Industry in My Town	(3)

Normal School and State Teachers' College Contest

The Relation of Chemistry to Health and Disease

ELINOR KRAUSHAAR	Northern State Teachers' College, Aberdeen, S. D.	Chemistry as an Aid to Surgery	(1)
WILLIAM CLAGGETT SELSAM	Indiana State Teachers' College, Terre Haute, Ind.	Synthetic Medicines	(2)
LAURENCE MORNINGSTAR	Western Illinois State Teachers' College, Macomb, Ill.	Relation of Chemistry to Health and Disease	(3)

The Relation of Chemistry to the Enrichment of Life

THELMA CHERRY	East Carolina Teachers' College, Greenville, N. C.	The Rôle of Chemistry in the Diffusion of Knowledge	(1)
AUGUSTA E. MILLER	State Teachers' College, Stevens Point, Wis.	How Chemistry Has Enriched Life in the Last Twenty-Five Years	(2)
HELEN RENICK	State Teachers' College, Slippery Rock, Penna.	How Chemistry Has Enriched Life in the Last Twenty-Five Years	(3)

The Relation of Chemistry to Agriculture or to Forestry

IRWIN PARRILL	Illinois State Normal University, Normal, Ill.	Utilization of By-Products in Agriculture	(1)
MILTON IRVING PERRY	Northern Illinois State Teachers' College, DeKalb, Ill.	Chemistry in Relation to the By-Products of Agriculture	(2)
RAY H. WRIGHT	Eastern Kentucky State Teachers' College, Richmond, Ky.	Fertilizers and Agriculture	(3)

The Relation of Chemistry to National Defense

MARGARET LOUISE BROWN	Northern State Teachers' College, Aberdeen, S. D.	Chemistry and Aviation	(1)
ISABEL AGNES FARR	State Teachers' College, Fredericksburg, Va.	Chemistry in Relation to Aviation	(2)
FRED DELOS BARBER	Illinois State Normal University, Normal, Ill.	Chemistry and Aviation	(3)

The Relation of Chemistry to the Home

ESTHER LILLIAN COLLIER ZALKAN	Farmington State Normal School, Farmington, Maine	Chemistry and Better Food	(1)

JUANITA WORSLEY	East Carolina Teachers' College, Greenville, N. C.	Chemistry and Household Conveniences	(2)
VLASTA BRACHTL	Chicago Normal College, Chicago, Illinois	Chemistry and Household Conveniences	(3)

The Relation of Chemistry to the Development of an Industry or a Resource of the United States

NEVILLE WRENN	West Texas State Teachers' College, Canyon, Texas	The Utilization of a Resource in a Major Chemical Industry in My Town	(1)
ARTHUR TIPTON	Eastern State Teachers College, Richmond, Ky.	The Relation of Chemistry to the Development of the Cellulose Industry	(2)
RALPH BATES	Illinois State Normal University, Normal, Ill.	The Utilization of a Resource in a Major Chemical Industry in My State	(3)

Laboratory Concentration of the Missouri Iron Ores of Iron Mountain and Pilot Knob. Two types of ores found associated with the igneous intrusions of Southeast Missouri have been studied to determine their amenability to concentration. Reserves of both ore deposits are large but both ores are too siliceous to be of value without beneficiation.

Petrographic studies as well as float-and-sink tests were made on each ore to determine its character. The results showed that high-grade concentrates accompanied by high recoveries would be difficult to obtain on either ore by gravity methods. Magnetic roasting tests were performed, and magnetic concentration methods were applied to the roasted ores. The results were encouraging and the optimum condition for carrying on the roasting operations and the magnetic concentration process were worked out.

The conclusions from the study of the Pilot Knob ore were that the locking between the iron minerals and the gangue was such that crushing to at least 150 mesh would be necessary to give a fair liberation. Gravity concentration would be impractical. Due to the fineness of the hematite and the porosity of the ore magnetizing roasting is easily performed. Magnetic concentration of roasted ore finer than 150 mesh should give concentrates satisfactorily low in silica, very low in phosphorus, and high in iron. The recovery of iron should be excellent.

Iron Mountain ore is a complex of minerals, the most important being hematite, garnet, quartz, and calcite. Due to the high specific gravity of the garnet, gravity concentration of this ore is difficult, and at best only a medium-grade concentrate can be produced. The hematite is dense, and for satisfactory magnetic roasting as a preliminary to magnetic concentration the ore must be previously crushed to a fine size or roasted at a temperature of 600°C. or more. Magnetic concentration of the roasted ore will give high recoveries and high-grade concentrates, provided that the ore treated is finer than 28 mesh.—*Bull. School of Mines & Metallurgy, University of Missouri, Rolla, Mo.*

Recent Books

Quantitative Pharmaceutical Chemistry. GLENN L. JENKINS, Ph.D., and ANDREW G. DUMEZ, Ph.D., professors in the School of Pharmacy, University of Maryland. McGraw-Hill Book Co., Inc., New York City, 1931. xxiii + 408 pp. 14.5 × 21.5 cm. 68 Figs. $3.50.

While conditions governing the practice of pharmacy in the United States have resulted in its commercialization to a very large extent, the pharmacist's work is based upon a considerable scientific foundation. There was a time when pharmacists were almost the only working chemists and they contributed a great deal to the development of chemistry in the formative period of that development, before 1850. These facts are exemplified in the nature and content of the book under review. Not all pharmacists practice analytical chemistry to the extent covered by this book, but a thorough study of the subject is a part of their training and a considerable number of pharmacists approach the practice of analytical chemistry through pharmacy.

Some idea of the pharmaceutical applications of quantitative analysis can be obtained from a brief outline of the contents of the book. After a statement of the scope of the subject, the book is divided into four parts. Under general chemical methods used in quantitative analysis of chemicals and drugs official in the United States Pharmacopeia and the National Formulary, we find general directions for analytical work, a few exercises on gravimetric methods; a thorough treatment of volumetric methods, including general principles of volumetric analysis, alkalimetry, acidimetry, precipitation, oxidation-reduction methods; gasometric methods and electrolytic methods. Under physical methods for the quantitative analysis of official chemicals and drugs, we find methods for the determination of solubility, specific gravity, melting, congealing and boiling points, refractive index, index of rotation, and viscosity. Under special methods used in quantitative analysis of official chemicals and drugs, we find methods for the determination of ash, moisture, extractive matter, constants of fats and oils, constituents of volatile oils, and enzymes, and several chapters on alkaloidal assay work. In the final section on special non-official methods, we find chapters on hydrogen-ion concentration, photometric methods, and ultimate analysis.

Like many books which cover both the theory and practice of a laboratory subject, this treatise combines laboratory manual, textbook and reference book between its covers and not all colleges of pharmacy would be able to allow in their crowded curricula the time necessary to cover the whole book.

The writer of this review is keenly aware of the need of a good book on this subject and a careful examination of this book convinces us that Messrs. Jenkins and DuMez have gone far to satisfy this need.

THEODORE J. BRADLEY
MASSACHUSETTS COLLEGE OF PHARMACY
BOSTON, MASSACHUSETTS

The Quantum Theory. FRITZ REICHE, Principal of Physics at the University of Breslau. Translated by H. S. HATFIELD, B.Sc., Ph.D., AND HENRY L. BROSE, M.A. Second edition, E. P. Dutton and Company, Inc., New York City, 1930. viii + 218 pp. 15 Figs. 12 × 18.5 cm. $2.10.

At the time of the appearance of its first edition this little book was one of the clearest and most useful guides available for those who were making their first acquaintance with the quantum theory. The second edition which now appears after a lapse of nine years is essentially the older book with a few changes and an additional chapter which discusses briefly the

revolutionary developments which have taken place in theoretical physics during this period of time.

There is still a great deal to be said for the historical approach to the quantum theory. The aspect of quantum mechanics changes so rapidly, almost daily, that those outside the field of action may well hesitate before making the effort necessary to understand the very recent developments. For those who wish to approach the problems of theoretical physics from the older point of view this book may be very useful. It presents the experimental evidence and the points of contact with the older theory which certainly are very important for a clear understanding of our modern theories, and which perhaps have received less emphasis than they should in some of the other recent books on the subject.

DONALD H. ANDREWS
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

Modern Textbook in Chemistry. J. ELLIS STANNARD, Instructor in Chemistry, Boys' High School, Brooklyn, N. Y. Academic Book Company, New York City, 1930. viii + 376 pp. 114 Figs. 13 × 19 cm. $1.32.

In his desire to avoid the Scylla of "cyclopedic treatment" which he believes to be confusing and discouraging to the young student, the author has fallen into Charybdis. He has written a chemical catechism which may meet fully the requirements "of the New York State Board of Regents, the College Entrance Examination Board, and the American Chemical Society" but it will please few chemistry teachers except the Gradgrinds, with their devotion to "Facts, Sir, nothing but Facts!" To lop off every item of interest outside the bare bones of a subject will not tend to make it palatable to the student, however admirable it may be in preparing for a Regents or College Entrance Examination. Not all chemistry teachers will kiss the clay feet of this pair of Collossi. And as sixty per cent of chemistry students probably do not go to college, perhaps they would enjoy some of the detail which the author omits.

If the illustrations "are used to teach chemistry, not merely to show machinery" we wonder that the picture of Dr. Millikan (Figure 21) is shown with the elaborate and unexplained glassware. But for the assurance of the title, the illustration of Open Pit Iron Ore Mining (Figure 93) might as well be that of Meteor Cañon. A flow sheet diagram would be an improvement over the titled bottles which are given several places. Incidentally, Michael Faraday is still washing glassware for Sir Humphry Davy. [See J. CHEM. EDUC., **7**, 859 (Apr., 1930).]

If the author had sought the golden mean between his own text and the extra long texts of which he complains, if he had included a list of supplementary reading, if he had been willing to have cracked a joke once in a while, his text would have been far more human, far nearer to the present objectives of chemical education.

This text will be quite useful to the crammers—to those who, in chemistry, as in other subjects, expect a docile repeating back of statements and opinions. But as a force in civilization, a way of livelihood for thousands of men, it fails to present live, every-day chemistry to the student.

R. E. BOWMAN
WILMINGTON TRADE SCHOOL
WILMINGTON, DELAWARE

The Carbon Compounds. C. W. PORTER, Professor of Chemistry, University of Southern California. Second revised edition. Ginn and Co., Boston, Mass., 1931. ix + 469 pp. 15 × 23 cm. $4.00.

The revised edition of Porter's well-known text adheres very closely to the plan of the first edition, and the changes in form are of minor importance. The introduction has been much abbreviated and the seventeen pages of the first edition's introduction shortened to seven by the omission of a considerable amount of material dealing with the electron theory.

Much new material has been incorporated in the work to bring it abreast of the

times. The work of Kendall and Harington on thyroxine, and the researches of Haworth and Hudson on structures of the carbohydrates, are mentioned, but in each instance the space devoted to this important work is so brief that the reader is left with no idea as to the methods employed by these investigators or the extent of their work. Only two references to Hudson's investigations are given, and in the text his researches are dismissed with three lines. The principle of optical superposition, on which much of Hudson's work is based, is not even mentioned. The section on disaccharides is particularly brief, and next to nothing is said about the contributions of Hudson and Haworth in this field.

The preparation of methyl alcohol from water gas is dismissed in four lines, and no mention is made at all of the importance of the process, or of the possibility of synthesizing other alcohols in a like manner. Indeed, one would be led to believe that the wood distillation industry is thriving, and that synthetic methanol is an unimportant substance.

The hydrogenation of petroleum is not mentioned, and "cracking" is very briefly dismissed. No mention of dehydrogenation as a means of preparing aldehydes and ketones catalytically is made. Certainly this excellent method deserves a few words in the most elementary text. The formation of bisulfite addition products from aldehydes and methyl ketones is given far too little space. The reader is left with the erroneous impression that the reaction takes place equally well with all methyl ketones. The reaction should be expressed as an equilibrium, and some mention should certainly be made of the effect of structure on the position of the equilibrium.

After a careful discussion of the equilibrium of the esterification process, no mention is made of the clever application of the principles involved in the preparation of ethyl acetate by continuous esterification. Similarly, no mention is made of the continuous distillation method for preparing absolute alcohol. A few words about a process illustrating such an important principle would be expected.

A considerable amount of space is devoted to essential oils, and the alkaloids. In view of the rather limited treatment given many more fundamental subjects, this fact makes the work seem unbalanced.

In accordance with the plan of the previous edition, the latter part of the book (87 pp.) is devoted to a discussion of general organic reactions. From a pedagogic standpoint it seems questionable practice in most cases to isolate this material from the previous discussion of the substances involved. In the section dealing with aldol condensation under aldehydes and ketones, no mention is made of the possibility of a ketone's taking part in a similar reaction, and unless the reader turns to the section at the end of the book on condensation reactions in general, he will obtain an erroneous impression. Even in this latter section, the treatment is extraordinarily brief, and one is left to infer the possibility of preparing diacetone alcohol. No mention at all is made of the possible connection of this sort of process in the building up of sugars.

The discussion of the Grignard Reaction contains no mention of the excellent work of Gilman and his co-workers on the effect of various variables on the yield of reagent. A great deal of space is devoted to the various reactions of the reagent, and about a half a page to the far more important problem of obtaining the reagent itself.

The author's interest in molecular rearrangements is evidenced by the sixteen-page section dealing with this important subject. The inclusion of certain rather unimportant rearrangements, however, seems out of place in a work of this size.

Following the text is an appendix in which are described methods of deducing formulas, etc., and finally a number of questions and problems.

The work could be used in a year's introductory course in organic chemistry but, in the estimation of the reviewer, it would

not be a suitable text for an advanced course.

References to the original literature are frequent, print and paper are good, and the binding is of excellent quality.

NATHAN L. DRAKE

UNIVERSITY OF MARYLAND
COLLEGE PARK, MD.

Organic Syntheses. Volume XI. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. CARL S. MARVEL, Editor-in-Chief; C. F. H. ALLEN, Secretary to the Board, McGill University, Montreal. John Wiley and Sons, Inc., New York City, 1931. vii + 106 pp. 15 × 23 cm. $1.75.

Organic chemists always welcome each new volume in this series, which has become one of the valuable contributions of America to this field of chemistry.

The present issue contains thirty-one preparations from some twenty laboratories, mainly university—among the foreign ones are found Freiburg, Münster, and Vienna. The list follows: Acrolein Acetal, α-Aminoisobutyric Acid, 1-Amino-2-Naphthol Hydrochloride, 1-Amino - 2 - Naphthol - 4 - Sulfonic Acid, Azoxybenzene, α-Bromoisovaleric Acid, Bromomesitylene, β-Chloropropionaldehyde Acetal, Citraconic Anhydride and Citraconic Acid, Cyanogen Bromide, 2,4-Diaminotoluene, Ethyl Ethylenetetracarboxylate, Ethyl Phenylcyanopyruvate, Ethyl Pimelate, Fumaric Acid, *dl*-Glyceric Aldehyde, *dl*-Glyceric Aldehyde Acetal, Haptaldoxime, *n*-Heptylamine, *p*-Iodoaniline, Isodurene, Itaconic Anhydride and Itaconic Acid, Mesaconic Acid, 3-Methyl Pentanoic Acid, α-Naphthoic Acid, *n*-Pentane, Symmetrical and Unsymmetrical *o*-Phythalyl Chlorides, *iso*-Propyl Thiocyanate, Thiobenzophenone, *o*-Toluic Acid, Triethyl Carbinol.

It might be noted that the syntheses of ethyl pimelate and fumaric acid are interesting illustrations of the formation of open chain derivatives from ring compounds.

The value of the preparations is twofold: not only do they afford approved methods for the synthesis of needed "ausgangsmaterial" but their study gives valuable hints as to the technic of organic reactions.

F. B. DAINS

UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

Qualitative Chemical Analysis. HERMAN T. BRISCOE, Professor of Chemistry, Indiana University. D. Van Nostrand Company, Inc., New York City, 1931. v + 279 pp. 29 Figs. 14 × 22 cm. $2.25.

Another book of qualitative analysis. Considering the limited number of elements whose detection is taken care of by the ordinary qualitative scheme it seems that the possible number of combinations and permutations would soon be reached. But, just as artists in ages past have been painting faces with a limited number of features and have produced no two alike, so analysts have written and are writing their qualitative texts and no two are alike. Each has some features that appeal to us, and some that do not. Some books like the masterpieces of art appeal favorably to the majority of us and are acclaimed a new step, a great advance.

Now, here is a new book built around the framework of the old familiar hydrogen sulfide separation. It contains preliminary experiments on each of the ions so that the beginner may learn what a certain precipitate ought to look like and how it ought to behave. It contains plenty of theoretical matter (142 pages) so that he may learn why and under what conditions a reaction occurs. As the author states in the preface, the methods and principles which make up the book are those which the author has used in his classes for many years. Also, the study of the theories and principles of electrolytic solutions serves as an introduction to physical chemistry for the chemistry major or as a source of knowledge of many of the most fundamental concepts of theoretical chemistry for the

student who will never take a course in physical chemistry. Altogether the book seems to be well worthwhile.

Some details which prospective adopters of the book may like to know are the following. The order of the analytical groups of cations begins with the alkali group. The copper and tin groups are separated by ammonium polysulfide. In many instances alternative procedures are given. Amplifying notes and review questions accompany the discussion of each group. Twenty-seven pages are devoted to the reactions of the anions and their separation and identification. The preliminary examination of the solid is limited to heating in a closed tube and treatment with concentrated sulfuric acid. Directions are given to remove organic matters and silicates, if present, before the analysis proper is begun. Phosphates and oxalates are to be detected and the effect of their presence neutralized by changes in the procedures of Group III.

CARL OTTO

UNIVERSITY OF MAINE
ORONO, MAINE

Food Analysis. Typical Methods and Interpretation of Results. A. G. WOODMAN, Associate Professor of Chemistry of Foods, Massachusetts Institute of Technology. Third edition, McGraw-Hill Book Co., Inc., New York and London, 1931. xii + 557 pp. 110 Figs. 14 × 20 cm. $3.50.

Since the publication of the first edition of Professor Woodman's Food Analysis in 1915 the book has established such an excellent reputation as to render superfluous any general review of the present edition. The author states that he has made practically no change in the plan of the book and has not attempted to include additional topics. Perusal of the book shows that the author has taken cognizance of improvements in methods which have occurred since the earlier edition of his book. The reviewer noticed, however, that the thiocyanogen-iodine number is not mentioned and that more recent determinations of the specific rotatory powers of certain sugars are not included in the tabulation on page 262. The factor for the conversion of degrees Ventzke to angular given on page 268 is strictly valid only for sucrose. In the discussion of the determination of starch there is no mention of the Rask method. In the discussion of the Roese-Gottlieb method for the determination of fat in milk, the reviewer feels that a brief description of the widely used Mojonnier apparatus should have been included.

The thorough discussions of analytical methods and interpretation of results in Professor Woodman's book are in a large measure responsible for the fact that it is one of the well-thumbed volumes in every food analyst's library.

ARTHUR W. THOMAS

COLUMBIA UNIVERSITY
NEW YORK CITY

Supervised Student-Teaching. ARTHUR RAYMOND MEAD, Head of Department of Education, Ohio Wesleyan University, and Sometime Visiting Professor of Education, Teachers' College, Columbia University. Johnson Publishing Co., New York, Chicago, etc., 1930. xxii + 891 pp. 13.25 × 20.25 cm. $3.00.

A comprehensive treatise dealing with the problems of the laboratory school and teacher-preparation in the United States. In twenty-five chapters the author summarizes the large and varied body of materials which he has collected since 1914 in connection with his service as chairman of the Committee on Practice Teaching of the Society of College Teachers of Education and as chairman of the Research Committee of the Supervisors of Student-Teaching. The volume is divided into three parts. *Part One* deals with introductory data, definitions of problems, and the basic theory involved. *Part Two* describes the work of the student-teacher; and *Part Three* is devoted to the larger problems of an administrative type such as the selection and assignment of student-teachers, the organization of laboratory

school work, coöperation with off-campus schools, and such important items as buildings, legal status, the functions of critics and directors, and the evaluation of student-teaching.

The book contains many well-selected tables and suggestive charts; there are a few illustrations of outstanding contributors in the field of teacher-training and of notable buildings in the educational field.

It is certain that this book will be a valuable aid to those engaged in training teachers for work in primary, elementary, secondary, and high-school positions. It is obviously not intended as an aid to those who are training teachers of chemistry, but the discussion of the advantages of learning to teach by participation and of the criticisms and dangers of such a plan cannot fail to be helpful.

B. S. HOPKINS
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

MISCELLANEOUS PUBLICATIONS

Record of Current Educational Publications, Comprising Publications from July–December, 1930. Compiled by MARTHA R. MCCABE, Library Division. *Bulletin*, 1931, *No. 3.*, U. S. Dept. Interior, Office of Education. U. S. Government Printing Office, Washington, D. C., 1931. (For sale by the Superintendent of Documents, Washington, D. C.) 118 pp. 15 × 23 cm. $0.20.

Biennial Survey of Education in the United States, 1928–30. Vol. 1. *Bulletin*, 1931, *No. 20*, U. S. Dept. Interior, Office of Education. U. S. Government Printing Office, Washington, D. C., 1931. (For sale by the Superintendent of Documents, Washington, D. C.) 15 × 23 cm. $0.05 each.

Chapter X. Hygiene and Physical Education. MARIE M. READY, Associate Specialist in Recreation, and JAMES FREDERICK ROGERS, M.D., Consultant in Hygiene and Specialist in Health Education. 27 pp.

Chapter XV. Medical Education. WILLARD C. RAPPLEYE, M.D., Director of Study, Commission on Medical Education. 14 pp.

Chapter XXI. Educational Boards and Foundations. HENRY R. EVANS, Editorial Division. 9 pp.

Bibliography on the Honor System and Academic Honesty in American Schools and Colleges. C. O. MATHEWS, Associate Professor of Education, Ohio Wesleyan University. *Pamphlet No. 16*, U. S. Dept. Interior, Office of Education. U. S. Government Printing Office, Washington, D. C., 1931. (For sale by the Superintendent of Documents, Washington, D. C.) 18 pp. 15 × 23 cm. $0.05.

Careers and Professions. U. S. Dept. Interior, Office of Education, Washington, D. C., 1930.

The Office of Education has issued a series of monographs by WALTER J. GREENLEAF, free upon request, on careers and professions. The numbers and titles of the circulars which have come to our attention are:

No. 19. Medical Education.
No. 20. Journalism.
No. 22. Legal Education.
No. 23. Librarianship.
No. 24. Architecture.
No. 25. Electrical Engineering.
No. 27. Civil Engineering.
No. 30. Mechanical Engineering.

As we conquer peak after peak we see in front of us regions full of interest and beauty, but we do not see our goal, we do not see the horizon: in the distance tower still higher peaks, which will yield to those who ascend them still wider prospects.—SIR JOSEPH JOHN THOMPSON

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